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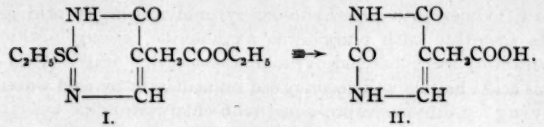
Contributions from the Sheffield Laboratory of Yale University.

CLIV.—RESEARCHES ON PYRIMIDINES: SYNTHESIS OF 4-METHYLURACIL-5-ACETIC ACID.

[TWENTY-EIGHTH PAPER.]

BY TREAT B. JOHNSON AND FREDERICK W. HEYL.

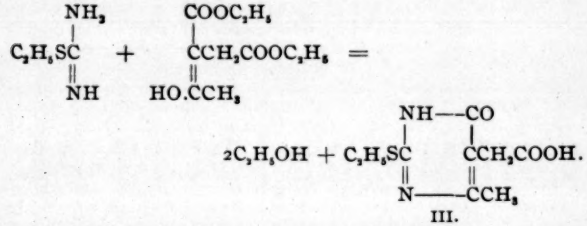
It was shown, in a previous paper from this laboratory,[1] that diethyl formylsuccinate condenses smoothly with pseudo-ethylthiourea, giving ethyl 2-ethylmercapto-6-oxypyrimidine-5-acetate (I.). When this pyrimidine was warmed with concentrated hydrochloric acid, it was converted quantitatively into thymine-5′-carboxylic acid (II.):



I. II.

Johnson and Speh: THIS JOURNAL, **38**, 602.

(1) 4-Methyluracil-5-acetic acid can be prepared in an analogous manner from pseudoethylthiourea and diethyl acetosuccinate.[1] They condense, in presence of an excess of alkali, giving a good yield of 2-ethylmercapto-4-methyl-6-oxypyrimidine-5-acetic acid (III.). The condensation can be represented by the following equation:



It is an interesting fact that the mercapto acid (III.) is obtained in this condensation, instead of the ethyl ester, as in the condensation with diethyl formylsuccinate.

(2) Ethylmercapto-4-methyl-6-oxypyrimidine-5-acetic acid (III.) was quantitatively converted into 4-methyluracil-5-acetic acid (VI.) when digested with concentrated hydrochloric acid. When an alcoholic solution of the mercapto acid (III.) was boiled with a small quantity of hydrochloric acid a mixture of ethyl 2-ethylmercapto-4-methyl-6-oxypyrimidine-5-acetate (IV.) and ethyl 4-methyluracil-5-acetate (V.) was obtained. The latter ester was also formed by esterifying the oxygen acid (VI.) with ethyl alcohol and sulphuric acid. 2-Amino-4-methyl-6-oxypyrimidine-5-acetic acid (VII.) was prepared by heating 2-ethylmercapto-4-methyl-6-oxypyrimidine-5-acetic acid (III.) with alcoholic ammonia.

2-Ethylmercapto-4-methyl-6-oxypyrimidine-5-acetic acid reacts smoothly with phosphorus oxychloride, giving 2-ethylmercapto-4-methyl-6-chlorpyrimidine-5-acetylchloride (VIII). This acid chloride was decomposed immediately by cold water, giving 2-ethylmercapto-4-methyl-6-chlorpyrimidine-5-acetic acid (XI.). 2-Ethylmercapto-4-methyl-6-chlorpyrimidine-5-acet-

[1] Fittig and Spencer: Ann. Chem. (Liebig), 283, 67.

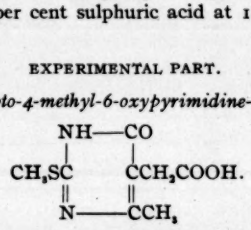
amide (IX.) was formed when the acid chloride was poured into cold alcoholic ammonia.

2-Ethylmercapto-4-methyl-6-chlorpyrimidine-5-acetic acid (XI.) is very stable in the presence of ammonia. It was recovered unaltered after heating with alcoholic ammonia at 120°. Treatment with ammonia at 135° gave 2-ethylmercapto-4-methyl-6-aminopyrimidine-5-acetic acid (XII.). When heated with alcoholic ammonia at 170°–180° the mercapto radical was also replaced by the amino group and 2,6-diamino-4-methylpyrimidine-5-acetic acid (X.) resulted. These different transformations are represented by the formulas on page 662.

4-Methyluracil-5-acetic acid (VI.) is less soluble in water than the thymine-5′-carboxylic acid (II.) described by Johnson and Speh.[1] It gives characteristic potassium, barium, and lead salts which crystallize from water with water of crystallization. The acid is not precipitated from its aqueous solution by barium chloride or phosphotungstic acid. It can be heated with 20 per cent sulphuric acid at 153°-173° without alteration.

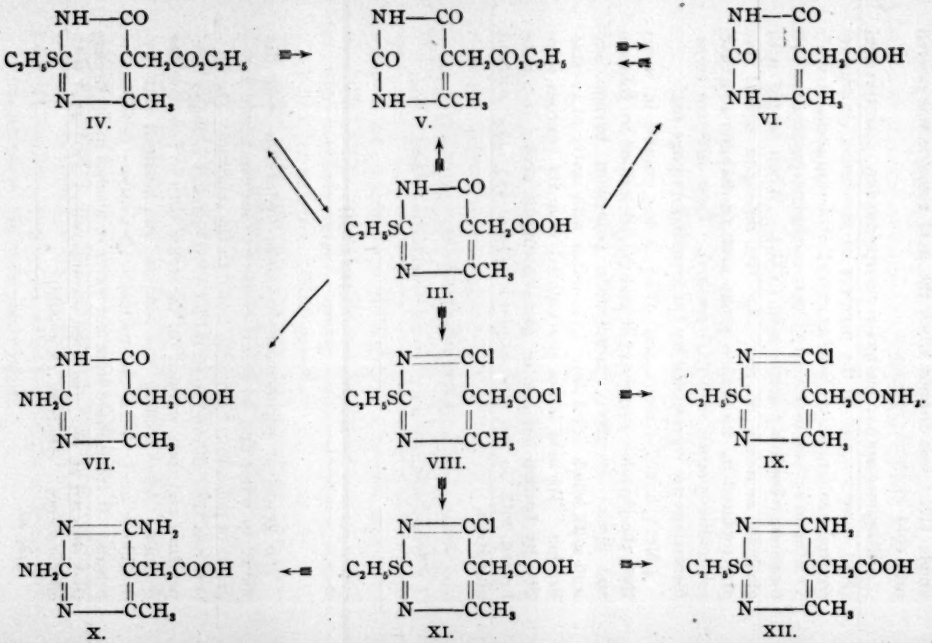
EXPERIMENTAL PART.

2-Methylmercapto-4-methyl-6-oxypyrimidine-5-acetic Acid,



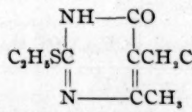
Ten grams of pseudomethylthiourea hydriodide were dissolved in water and 10 grams of diethyl acetosuccinate and 5 grams of potassium hydroxide added to the solution. The mixture was then allowed to stand for 8–10 hours at ordinary temperature and then warmed on the steam bath to complete the reaction. After cooling, the solution was acidified with hydrochloric acid, when the mercapto derivative deposited in prisms. It crystallized from hot water or alcohol in flat prisms that sintered at 260° and then decomposed at 270°–272° with effervescence. Analysis (Kjeldahl):

[1] *Loc. cit.*


NH—CO
C2H5SC CCH2CO2C2H5
N—CCH3
IV.
NH—CO
CO CCH2CO2C2H5
NH—CCH3
V.
NH—CO
CO CCH2COOH
NH—CCH3
VI.
NH—CO
C2H5SC CCH2COOH
N—CCH3
III.
NH—CO
NH2C CCH2COOH
N—CCH3
VII.
N=CCl
C2H5SC CCH2COCl
N—CCH3
VIII.
N=CCl
C2H5SC CCH2CONH2
N—CCH3
IX.
N=CNH2
NH2C CCH2COOH
N—CCH3
X.
N=CCl
C2H5SC CCH2COOH
N—CCH3
XI.
N=CNH2
C2H5SC CCH2COOH
N—CCH3
XII.

	Calculated for $C_8H_{10}O_3N_2S$.	Found. I.	II.
N	13.08	13.14	13.06

2-Ethylmercapto-4-methyl-6-oxypyrimidine-5-acetic Acid,



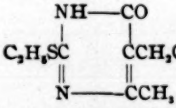
The best yield of this pyrimidine was obtained when we proceeded under the following conditions: Thirty-five grams of the hydrobromide of pseudoethylthiourea were dissolved in about 250 cc. of cold water and 43 grams of diethyl acetosuccinate stirred into the solution. Twenty-two grams of potassium hydroxide were then added, when a clear solution resulted. This was then allowed to stand overnight at ordinary temperature and finally heated on the steam bath for one hour. After cooling and shaking with ether to remove any unaltered diethyl acetosuccinate, an excess of acetic acid was added, when the mercaptopyrimidine deposited in granular, prismatic crystals. The yield was 19 grams, corresponding to about 72 per cent of the theoretical. In a second condensation we obtained 4.2 grams of the mercaptopyrimidine from 8 grams of the pseudourea hydrobromide and 10 grams of diethyl acetosuccinate. This pyrimidine is practically insoluble in cold, and sparingly soluble in hot, water. It deposited from boiling 95 per cent alcohol in blocks. It dissolved in boiling benzonitrile and nitrobenzene and separated from both of these solvents, on cooling, in elongated prisms. The decomposition point varies with the rate of heating, but it usually decomposed at about 255°, evolving carbon dioxide and ethylmercaptan. Analysis (Kjeldahl):

	Calculated for $C_9H_{12}O_3N_2S$.	Found. I.	II.
N	12.28	12.55	12.30

Potassium Salt, $C_9H_{11}O_3N_2SK$.—This salt is extremely soluble in cold water. It crystallized from 50 per cent alcohol in microscopic needles. Analysis (Kjeldahl):

	Calculated for $C_9H_{11}O_3N_2SK$.	Found. I.	Found. II.
N	10.52	10.67	10.45

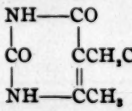
Ethyl 2-Ethylmercapto-4-methyl-6-oxypyrimidine-5-acetate,



This ester was not obtained as a product of the preceding condensation. This is explained by the fact that it was necessary to use an excess of potassium hydroxide to keep the diethyl acetosuccinate in solution and the ester, if formed, was always saponified. It was prepared by boiling the mercapto acid in alcoholic solution with a few drops of sulphuric acid. Two grams of the mercapto acid, 25 cc. of absolute alcohol, and 2 cc. of concentrated sulphuric acid were digested on the steam bath for 5 hours. The excess of alcohol was then evaporated at ordinary temperature, when we obtained an oily residue with some colorless, prismatic crystals in suspension. These were filtered by suction and the syrup again allowed to stand for a few hours, when a second crop was obtained. The yield was 0.25 gram and the compound was identified as 4-methyluracil-5-ethylacetate (see below). The syrup was treated with 20–30 cc. of cold water, when a crystalline compound deposited which melted at 151°–163° to a clear oil. It deposited from 95 per cent alcohol in hairlike crystals that melted at 163°–165° to a clear oil. It gave a test for sulphur. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{16}O_3N_2S$.	Found. I.	Found. II.
N	10.93	11.4	11.08

4-Methyluracil-5-acetic Acid,



2-Ethylmercapto-4-methyl-6-oxypyrimidine-5-acetic acid dissolves at once in cold, concentrated hydrochloric acid and the

solution can be evaporated to dryness on the steam bath and the acid recovered unaltered. A quantitative yield of the oxygen acid was obtained, nevertheless, by boiling the mercapto-pyrimidine with concentrated hydrochloric acid until the evolution of ethylmercaptan ceased. It deposited from the boiling acid solution as a heavy, granular powder. The acid is practically insoluble in boiling alcohol and insoluble in cold water. It crystallized from hot water in long, transparent prisms that sintered at about 329° and decomposed at 340° (Anschütz thermometer) with violent effervescence. Bromine does not react with the acid in acetic acid solution at ordinary temperature. Analysis:

I. 0.1950 gram of substance gave 0.3274 gram of CO_2 and 0.0787 gram of H_2O.

II. 0.2352 gram of substance gave 0.3935 gram of CO_2 and 0.0955 gram of H_2O. Nitrogen (Kjeldahl):

	Calculated for $C_7H_8O_4N_2$.	Found. I.	II.	III.	IV.
C	45.65	45.77	45.62	.....	.....
H	4.34	4.48	4.50	.....	.....
N	15.21	....	....	15.09	15.10

Solubility in Water at 25°.—One hundred grams of water dissolved:

I.	II.
0.0901 gram acid	0.0894 gram acid

Potassium Salt of 4-Methyluracil-5-acetic Acid, $C_7H_7O_4N_2K \cdot 3H_2O$, was prepared by dissolving the acid in water with one molecular proportion of potassium hydroxide. The salt was extremely soluble in water but crystallized from very concentrated solutions in prismatic crystals. They contained water of crystallization which was determined by heating the salt at 105°–125° for 5 hours.

0.8455 gram of the salt lost 0.1544 gram H_2O.

	Calculated for $C_7H_7O_4N_2K \cdot 3H_2O$.	Found.
H_2O	19.5	18.26

Nitrogen determination for anhydrous salt (Kjeldahl):

	Calculated for $C_7H_7O_4N_2K$.	Found.
N	12.60	12.42

Silver Salt of 4-Methyluracil-5-acetic Acid, $C_7H_7O_4N_2Ag$.—When the potassium salt described above was dissolved in water and a molecular proportion of silver nitrate added, a gelatinous silver salt deposited. It was insoluble in boiling water and did not assume a crystalline form. Analysis for silver:

	Calculated for $C_7H_7O_4N_2Ag$.	Found.
Ag	37.11	40.00

Barium Salt of 4-Methyluracil-5-acetic Acid, $(C_7H_7O_4N_2)_2Ba.H_2O$.—When the calculated proportions of the acid and barium chloride were dissolved in hot water and the solution cooled, the unaltered acid separated. The salt was prepared by dissolving the potassium salt in water and adding the calculated amount of barium chloride. The salt separated, on cooling, in small prisms which were dried for analysis in a desiccator over sulphuric acid. It contained one molecule of water of crystallization which was determined by heating for 2 hours at 110°–136°.

0.8114 gram of salt lost 0.0300 gram of H_2O.

	Calculated for $(C_7H_7O_4N_2)_2Ba.H_2O$.	Found.
H_2O	3.45	3.69

Nitrogen determination for anhydrous salt (Kjeldahl):

	Calculated for $(C_7H_7O_4N_2)_2Ba$.	Found.
N	11.12	11.05

Lead Salt of 4-Methyluracil-5-acetic Acid, $(C_7H_7O_4N_2)_2Pb.H_2O$.—This salt was obtained as an insoluble crystalline powder when lead acetate was added to a solution of the acid. It crystallized from water in glistening plates or flat prisms which were dried for analysis in a desiccator over sulphuric acid. It contained one molecule of water of crystallization which was determined by heating at 117°–125° for 4 hours.

1.2847 grams of salt lost 0.0377 gram H_2O.

	Calculated for $(C_7H_7O_4N_2)_2Pb.H_2O$.	Found.
H_2O	3.04	2.93

Analysis of the anhydrous salt:

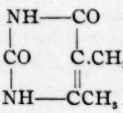
0.2594 gram substance gave 0.2769 gram CO_2 and 0.0583 gram H_2O. Nitrogen (Kjeldahl):

	Calculated for $(C_7H_7O_4N_2)_2Pb$.	Found. I.	II.	III.
C	29.32	29.12	....	....
H	2.44	2.49	....	....
N	9.77	....	10.00	9.73

Action of 20 Per Cent Sulphuric Acid.—The acid was recovered unaltered after heating with sulphuric acid for 2 hours at 153°–173°. When crystallized from water it decomposed at 340°. Analysis (Kjeldahl):

	Calculated for $C_7H_8O_4N_2$.	Found. I.	II.	III.
N	15.21	15.31	15.32	15.17

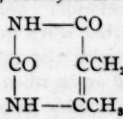
Ethyl Ester of 4-Methyluracil-5-acetic Acid,



This ester was obtained as a secondary product when we esterified 2-ethylmercapto-4-methyl-6-oxypyrimidine-5-acetic acid. It was easily obtained in pure condition by esterifying the oxygen acid in the usual manner. It crystallized from 95 per cent alcohol in needles that melted at 221°–222° to a clear oil. Analysis (Kjeldahl):

	Calculated for $C_9H_{12}O_4N_2$.	Found.
N	13.20	13.12

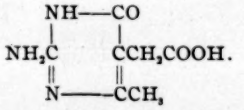
Methyl Ester of 4-Methyluracil-5-acetic Acid,



This ester deposited from methyl alcohol in fine needles that decomposed at 280°–282°. Analysis (Kjeldahl):

	Calculated for $C_8H_{10}O_4N_2$.	Found. I.	II.
N	14.14	14.10	14.4

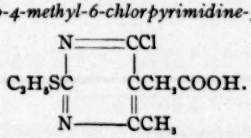
2-Amino-4-methyl-6-oxypyrimidine-5-acetic Acid,



Four grams of 2-ethylmercapto-4-methyl-6-oxypyrimidine-5-acetic acid were heated with alcoholic ammonia for 4 hours at 170°–180°. When the tube was opened there was some pressure, and the odor of ethylmercaptan was apparent. The solution was evaporated to dryness and the crystalline residue purified by recrystallization from water. It deposited in needles that decomposed at 322° with effervescence. Analysis (Kjeldahl):

	Calculated for $C_7H_9O_3N_3$.	Found. I.	II.
N	22.95	23.3	23.2

2-Ethylmercapto-4-methyl-6-chlorpyrimidine-5-acetic Acid,

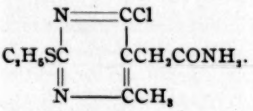


Ten grams of 2-ethylmercapto-4-methyl-6-oxypyrimidine-5-acetic acid and 50 cc. of phosphorus oxychloride were warmed on the steam bath until the evolution of hydrochloric acid gas practically ceased (2 hours). A dark colored solution was obtained. This was slowly poured upon crushed ice to decompose the excess of phosphorus oxychloride. No insoluble material deposited after this treatment, but when the acid solution was neutralized with sodium hydroxide the chloride separated in slender needles which dissolved again when an excess of alkali was added. The chloride was soluble in boiling benzene but insoluble in cold benzene; very soluble in alcohol. It was purified for analysis by recrystallization from hot water and depos-

ited in needles that melted at 118°–119° with evolution of carbon dioxide. The yield was good. Analysis (Kjeldahl):

	Calculated for $C_9H_{11}O_2N_2SCl$.	Found. I.	Found. II.
N	11.35	11.53	11.56

2-Ethylmercapto-4-methyl-6-chlorpyrimidine-5-acetamide,

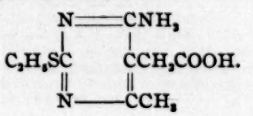


2-Ethylmercapto-4-methyl-6-oxypyrimidine-5-acetic acid was digested with an excess of phosphorus oxychloride until the evolution of hydrochloric acid gas ceased. Instead of being poured into water as in the previous experiment, this solution was poured slowly into a large volume of cold, alcoholic ammonia. The excess of alcohol and ammonia was then evaporated and the residue triturated with cold water to dissolve ammonium chloride. We obtained a crystalline compound that was insoluble in cold water but crystallized from hot water in sheaves that decomposed at 167°. The compound was very soluble in hot alcohol but can be crystallized from 50 per cent alcohol and from benzene. It was insoluble in dilute sodium hydroxide solution. Analysis (Kjeldahl):

	Calculated for $C_9H_{12}ON_2SCl$.	Found. I.	Found. II.
N	17.10	17.5	17.4

Action of Alcoholic Ammonia on 2-Ethylmercapto-4-methyl-6-chlorpyrimidine-5-acetic Acid.—The mercaptopyrimidine was recovered unaltered after heating with strong, alcoholic ammonia for 2 hours at 85°–95° and again for 3 hours at 110°–120°.

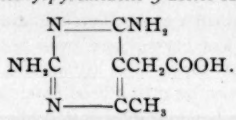
Action at 125°–135°: Formation of 2-Ethylmercapto-4-methyl-6-aminopyrimidine-5-acetic Acid,



Two and five-tenths grams of the chloride were heated with alcoholic ammonia for 2.5 hours at 125°–135°. When the tube was opened there was some pressure and a small amount of colorless, crystalline material was suspended in the alcohol. This was identified as the ammonium salt of 2-ethylmercapto-4-methyl-6-aminopyrimidine-5-acetic acid. The free acid was obtained by triturating the salt with dilute acetic acid. It deposited from 95 per cent alcohol in beautiful needles that melted sharply at 221°. They gave tests for sulphur and chlorine. This reaction was not smooth and the yield of the amino derivative was poor. When the alcoholic filtrates were evaporated to dryness a crystalline residue deposited. This proved to be a mixture from which nothing sufficiently pure for analysis was isolated. Analysis (Kjeldahl):

	Calculated for $C_9H_{13}O_2N_3S$.	Found.
N	18.50	18.64

2,6-Diamino-4-methylpyrimidine-5-acetic Acid,



This base was prepared by heating 2-ethylmercapto-4-methyl-6-chlorpyrimidine-5-acetic acid with alcoholic ammonia for 2 hours at 167°–180°. When the tube was opened there was much pressure, and a crystalline compound had deposited from the alcohol. This crystallized from hot water in small prismatic crystals that melted at 279°–280° with effervescence, turning brown at about 270°. It did not give tests for sulphur and chlorine, and dissolved in alkali and acids. Analysis (Kjeldahl):

	Calculated for $C_7H_{10}O_2N_4$.	Found.
N	30.77	30.61

NEW HAVEN, CONN.,
July 6, 1907.

Contributions from the Chemical Laboratory of the University of Illinois.

ON AMALGAMS: THE HYDRARGYRIDES OF THE ALKALI AND ALKALI EARTH METALS.

By George McPhail Smith.

The following methods, of which the first three are the more generally applicable, have been employed in the preparation of amalgams:

1. The electrolysis of a salt solution with a mercury cathode.
2. The action of an amalgam on a salt solution.
3. Directly from the metals.
4. The electrolysis of a suitable salt of mercury, with the metal to be amalgamated as cathode.
5. The action of a metal on the solution of a salt of mercury.
6. The action of mercury on a salt solution.

If the metals are arranged according to their tendency to amalgamate with mercury, they fall into three classes, as follows:

I. Metals which amalgamate with mercury with the formation of chemical compounds. This class includes the alkali and alkali earth metals[1] and thallium.[2] The solid amalgams are to be regarded as analogous to hydrated salts, *i. e.*, as being made up of a fundamental compound of mercury and the second metal, combined with various amounts of "mercury of cystallization."[3] The liquid amalgams are solutions of the solid amalgams in mercury; in them the amalgamated metal is not present in the monatomic condition, but the liquid amalgams are solutions in mercury of compounds of the general formula $mHg_{m'}$ containing only 1 atom of the amalgamated metal to the molecule.[4]

II. Metals which have a pronounced tendency to amalgamate directly with mercury, but which are not definitely known to enter into chemical combination with it. While not present

[1] Berthelot: Ann. Chim. Phys., [5], **18**, 442 (1879). Kerp: Z. anorg. Chem., **17**, 284 (1898). Kerp and Böttger: *Ibid.*, **25**, 1 (1900). Maey: Z. physik. Chem., **29**, 119 (1899). Guntz and Ferée: Compt. rend., **131**, 182 (1900). Kurnakoff: Z. anorg. Chem., **23**, 439 (1900). Haber and Sack: Z. Elek. Chem., **8**, 245 (1902).

[2] Kurnakoff and Puschin: Z. anorg. Chem., **30**, 86 (1902).

[3] Berthelot, Kerp, Böttger, Kurnakoff, and Maey: *Loc. cit.*

[4] Haber and Sack: *Loc. cit.* Haber: Z. physik. Chem., **41**, 399 (1902). Smith: This Journal, **36**, 124 (1906); **37**, 506 (1907).

to any great extent in the liquid phase, they nevertheless readily form solid solutions or isomorphous mixtures with mercury.[1] This class includes copper, silver, and gold, zinc and cadmium, gallium[2] and tin,[3] lead, antimony, and bismuth, also, judging from their positions in the periodic system, probably indium and germanium. Beryllium, magnesium, and aluminium form a transition to the next class.

III. Metals which at most have only a very slight tendency to amalgamate with mercury. To this class belong all other metals that have been investigated in this direction—notably the transitional elements of the eighth group of the periodic system.

From the following figures,[4] which give the amounts of metal present in 100 grams of saturated liquid amalgam, some idea may be had as to the relative solubility of the metals in mercury. It should be borne in mind, however, that the alkali and alkali earth metals are not present in the mercury in the free state.

Temperature.	Li	Na	K	Rb	Sr	Ba	Cu	Ag
0°	0.04	0.53	0.31	0.92	0.73	0.15	. .	. .
20°	. .	. .	0.47	. .	1.02	0.32	0.001	0.03
25°	. .	0.65	0.53	1.37	. .	0.34	. .	. .

	Au	Sn	Bi	Pb	Zn	Cd	Fe
0°	. .	. .	. .	. .	. .	. .	. .
20°	0.13	0.6	1.2	1.3	1.8	4.0	none
25°	. .	. .	. .	. .	. .	. .	. .

The Alkali and Alkali Earth Hydrargyrides.

The metals of the alkali and alkali earth groups, inclusive of ammonium[5] and probably exclusive of beryllium and magnesium, are capable of forming chemical compounds (hydrargyrides) with mercury. In the periodic system, beryllium and magnesium occupy positions in the second group that correspond to those

[1] Puschin: Z. anorg. Chem., **36**, 201 (1903).

[2] Ramsay: J. Chem. Soc., **55**, 521 (1889).

[3] See, however, Van Heterin [Z. anorg. Chem., **42**, 129(1904)], who claims the existence of a Sn-Hg compound.

[4] Kerp and Böttger: *Loc. cit.* Gouy: J. de Phys., **4**, 320 (1895). Gouy's figures for Cu and the metals following are for the "ordinary temperature," *i. e.*, probably about 20°.

[5] Smith: J. Am. Chem. Soc., **29**, June, 1907.

occupied by lithium and sodium in the first group. Lithium and sodium undoubtedly form compounds with mercury. But while very dilute beryllium[1] and magnesium amalgams can be prepared electrolytically from aqueous solutions, they are nevertheless very unstable; they decompose water with such ease, as compared with the amalgams of the more active alkali and alkali earth metals, that it is hardly to be assumed that these metals are in combination with the mercury.

In a previous investigation,[2] the stability of the alkali earth hydrargyrides was found to increase with the atomic weight (*i. e.*, with the chemical activity) of the alkali earth metal. In the case of the common alkali metals, however, this was found to be different; here the stability increases in the order: Li, K, Na. Among the alkali metals, sodium is in many respects quite independent in its behavior, and for this reason it was thought of interest to extend the investigation to rubidium and caesium, especially as according to the only statement the writer has been able to find on the subject[3] their amalgams are more readily oxidized than potassium amalgam, that they decompose water very readily, and that the amalgams are electropositive in the order: +Cs, Rb, K—. These statements owe their existence, in part at least, to the erroneous idea that the alkali metals exist in solution in mercury in the monatomic condition, just as they do in the gaseous state.[4]

Since potassium, rubidium, and caesium form a closely related triad, occupying in the first group of the periodic system a position corresponding to that of calcium, strontium, and barium in the second group, it was to be expected that their hydrargyrides would also increase in stability with increasing atomic weight of the alkali metal. Such, indeed, has been found to be the case.

EXPERIMENTAL PART.

Liquid amalgams of sodium, potassium, rubidium, and caesium were prepared by the electrolysis of solutions of the correspond-

[1] Ramsay: *Loc. cit.*, p. 530.
[2] This Journal, **37**, 506–542 (1907).
[3] Erdmann: Lehrb. d. anorg. Chem., 1902, p. 508.
[4] Erdmann: Z. anorg. Chem., **32**, 404 (1902).

ing chlorides. In each case the solution was placed in a small beaker containing mercury which was made the cathode by contact with a short platinum wire fused into the end of a glass tube. A little mercury in this tube served to connect the platinum wire with the negative copper wire of the circuit. The anode was a strip of platinum foil bent at a right angle, so that most of its surface was parallel with and close to that of the mercury. The current strength was 4 amperes at 6 volts, and the electrolysis was continued 10 minutes for each 100 grams of mercury taken, except in the case of the caesium. A great deal of heat was evolved in each case, but the evolution of hydrogen from the cathode was slight. It was, however, found necessary to stir the cathodes occasionally, in order to prevent the formation of a crust of the lighter crystalline amalgam at the surface. This would have given rise to a rapid evolution of hydrogen and greatly reduced the current efficiency. The amalgams thus prepared, were found to contain 0.25, 0.42, 0.90 and 0.95 per cent of Na, K, Rb, and Cs, respectively. The caesium amalgam was not made more concentrated for fear it might tend to solidify.

The mercurial solutions thus prepared were subjected to the action of air, water, and aqueous ammonia, and also to the action of three equivalent solutions containing equimolecular quantities of NaCl and KCl, NaCl and RbCl, and NaCl and CsCl, respectively. From their behavior under these conditions, conclusions could be drawn as to the relative stability of the alkali amalgams.

I. The Action of Air.

The amalgams were shaken in portions of 25 grams in dry, tightly stoppered 100 cc. bottles containing air. After a short time they began to stick to the sides of the bottles, and visibly to become oxidized. Caesium amalgam appeared, at first sight, to oxidize most rapidly, with rubidium, potassium, and sodium amalgams following in the order named. That this order was only apparent, however, will be shown below. In order to find whether any alkali nitride was formed by the action of air, the oxidized amalgams were treated with cold water and the filtered solutions tested with Nessler's reagent. No am-

monia was found. On the addition of water to the oxidized potassium, rubidium, or caesium amalgam, hydrogen peroxide was formed and a gas was rapidly evolved. This was found to be oxygen. The dioxides of these metals, KO_2, RbO_2, and CsO_2, were therefore present, and not the suboxide, as was stated for potassium in a former paper.[1] In consequence of the formation of hydrogen peroxide, the following comparative tests were made:

Twenty-five grams (*i. e.*, an excess) of each of the amalgams were shaken with air in a dry 100 cc. bottle as before, and, after the inside walls were completely coated with the amalgams, the stoppered bottles were allowed to stand overnight. The next morning 100 cc. of cold, dilute sulphuric acid were added to the contents of each bottle and the solutions decanted from the excess of amalgam and filtered from the finely divided mercury present. An excess (25 cc.) of a dilute solution of titanium sulphate was then added to each solution. The caesium solution changed to an orange color, the rubidium and potassium solutions to a deep, reddish orange, and the sodium solution remained uncolored. Ten cc. of each of the colored solutions were then diluted to 50 cc. and the colors compared in Nessler tubes. The equicolored columns were found to be 3.1 cm., 3.4 cm., and 9.3 cm. in height for the potassium, rubidium, and caesium solutions, respectively. Since the hydrogen peroxide was formed according to the equation $2MO_2+2H_2O=2MOH+H_2O_2+O_2$, it follows that the amalgams were oxidized with decreasing readiness in the order: K, Rb, Cs. At first sight the caesium amalgam appeared to be oxidized most rapidly because caesium dioxide is darker in color than either of the others. The oxidized potassium amalgam was a dull metallic gray in appearance, the rubidium amalgam a dull brownish gray, and the oxidized caesium amalgam resembled peacock copper ore (bornite) in color.

II. The Action of Water.

In these experiments, which were performed simultaneously with potassium, rubidium, and caesium amalgams, in quantities

[1] This Journal, **37**, 512 (1907).

of 27.5, 27.0, and 27.5 grams, respectively, the amalgams were placed in small watch glasses which were supported on a porcelain platform in the center of a heavy 3 liter glass beaker, filled with water at 20°. The watch glasses were each covered with an inverted funnel, the shortened stem of which projected into a graduated eudiometer tube filled with water. Starting with the eudiometer tubes filled and clamped in an inverted position in the water, it was found easy to introduce the watch glasses containing the amalgams and set the apparatus in position without the loss of any hydrogen. In every case the reaction started at a very low initial velocity and gradually became more rapid. This acceleration was due, as will be shown below, to traces of impurity in the water used (the ordinary distilled water of the laboratory). The readings that follow are a trifle too low, owing to the fact that a little hydrogen clung to each of the funnels. The error, however, is practically the same in each case.

Potassium Amalgam.

Hydrogen evolved. cc.	Minutes.	Hydrogen evolved. cc.	Minutes.	Hydrogen evolved. cc.	Minutes.
4.5	15	25.5	50	34.1	85
9.3	20	27.2	55	34.4	90
12.8	25	28.8	60	34.5	95
16.0	30	30.5	65	34.55	100
18.2	35	31.8	70	.....	
21.2	40	32.7	75	.....	
22.5	45	33.5	80	35.4 cc. = final volume	

Rubidium Amalgam.

Hydrogen evolved. cc.	Minutes.	Hydrogen evolved. cc.	Minutes.	Hydrogen evolved. cc.	Minutes.
4.0	15	22.4	55	31.5	95
8.0	20	23.9	60	32.5	100
11.2	25	25.9	65	32.9	105
13.8	30	26.2	70	33.4	110
16.0	35	27.4	75	33.7	115
18.0	40	28.6	80	34.0	120
19.6	45	29.7	85	.....	
20.9	50	30.7	90	35.1 cc. = final volume	

Caesium Amalgam.

Hydrogen evolved. cc.	Minutes.	Hydrogen evolved. cc.	Minutes.	Hydrogen evolved. cc.	Minutes.
0.8	15	4.7	55	10.1	95
1.1	20	5.4	60	10.8	100
1.45	25	6.1	65	11.5	105
1.9	30	6.7	70	12.0	110
2.4	35	7.3	75	12.8	115
2.8	40	8.1	80	...	
3.4	45	8.8	85	...	
4.0	50	9.4	90	22.3 cc. = final volume	

These figures are plotted graphically in Fig. I. They show that the liquid amalgams of these metals evolve hydrogen from water with decreasing velocity in the order: K, Rb, Cs.

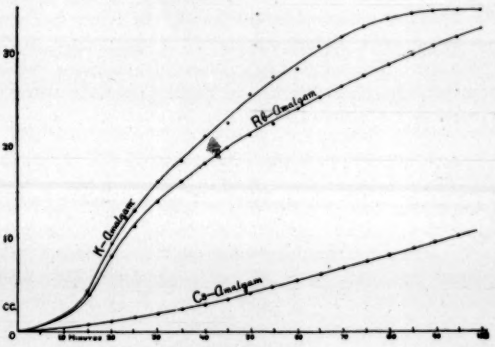


Fig. I.

Attention should be called to the fact that the presence of traces of certain impurities, especially iron or aluminium, in the water has a decided accelerating influence on the rate of evolution of hydrogen by these amalgams. According to the writer's experience, this influence is especially pronounced in the case of sodium amalgam.[1] With the water employed

[1] See, *e. g.*, under IV. B, below.

above, 27 grams of sodium amalgam evolved 11.2 cc. of hydrogen in 15 minutes, while with redistilled, ammonia-free water 27.5 grams of the same amalgam evolved only 0.3 cc. hydrogen in the same time. With the redistilled water 27.5 grams of sodium amalgam evolved 0.75 cc. of hydrogen in 55 minutes, while 26 grams of potassium amalgam evolved 0.8 cc. of hydrogen in the same time.

III. The Action of Aqueous Ammonia.

In these experiments the amalgams were put into test tubes, in portions of 1 cc., and to each amalgam 5 cc. of aqueous ammonia (sp. gr. 0.9) were added. The test tubes were loosely stoppered and then surrounded by larger, inverted test tubes. They were allowed to stand at room temperature. In proportion as ammonium, from the ammonium hydroxide contained in the solution, entered the amalgams, the latter became inflated, owing to the decomposition of the ammonium amalgam thus formed. The more rapidly inflated amalgams displaced ammonium from the solution more rapidly than the others, and can therefore be regarded as least stable.

Potassium Amalgam.

Hours	0.5	2	16	24	40	60	72
Volume (cc.)	2.2	3.5	6.0	6.5	6.5	5.5	1.3

Rubidium Amalgam.

Hours	0.5	2	16	24	40	64	70	90
Volume (cc.)	1.1	1.5	4.0	4.5	4.8	5.0	5.0	1.0

Caesium Amalgam.

Hours	0.5	2	16	24	40	64	70	90	96	100
Vol. (cc.)	1.0	1.2	2.5	3.2	4.0	4.7	4.8	5.0	2.0	1.0

These results are plotted graphically in Fig. II. They show that the amalgams displace ammonium with decreasing activity in the order: K, Rb, Cs. Sodium amalgam at ordinary temperature evolves hydrogen continuously, at constant volume, with the same solution.

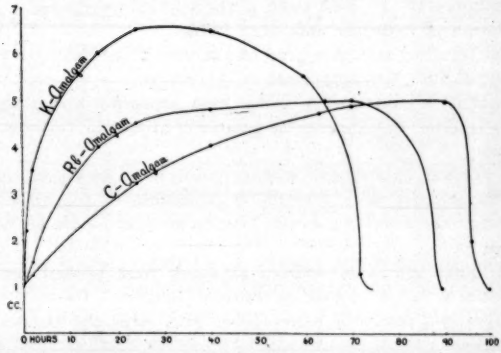


Fig. II.

IV. The Action of Equivalent Solutions Containing Equimolecular Quantities of Sodium Chloride and Potassium, Rubidium, or Caesium Chloride.

In these experiments each of the amalgams in the three pairs Na and K, Na and Rb, and Na and Cs, was acted upon by the corresponding solution, and in every case an equilibrium was found to exist, which was attainable in either direction. Such compounds[1] as Jänecke's $NaKHg_2$ could hardly be formed here, owing to the large excess of mercury present. The amalgams were washed and analyzed as described in an earlier paper.[2]

A. Potassium and Sodium.

The Action of Potassium, Sodium, and Lithium Amalgams on a Solution Containing Equimolecular Quantities of Sodium and Potassium Chlorides.—The solution employed was made by dissolving a mixture of 11.70 grams of sodium chloride and 14.92 grams of potassium chloride in water and diluting the solution to 100 cc.

(*a*) Fifty grams of potassium amalgam were treated for

[1] Z. physik. Chem., **57**, 507 (1907).
[2] This Journal, **37**, 514f.

30 minutes, at 24°, with 50 cc. of the solution mentioned. The evolution of hydrogen was very feeble.

The resulting amalgam gave, on analysis, KCl + NaCl = 0.3299 gram; K_2PtCl_6 = 0.3173 gram.

That is, it contained 0.05089 gram potassium and 0.09177 gram sodium; or, expressed in number of atoms, K : Na = 24.61 : 75.39.

A previous experiment[1] with 50 grams of an amalgam, made by the addition of 1.5 grams of potassium to 500 grams of mercury, and 50 cc. of a similar solution gave, in atoms, K : Na = 24.30 : 75.70.

(*b*) Fifty grams of sodium amalgam were treated for 30 minutes, at 24°, with 50 cc. of the same solution. The evolution of hydrogen was still more feeble than with the potassium amalgam.

The resulting amalgam gave, on analysis, KCl + NaCl = 0.3166 gram; K_2PtCl_6 = 0.2846 gram.

That is, it contained 0.04564 gram potassium and 0.09046 gram sodium; in atoms, K : Na = 22.90 : 77.10.

A previous experiment[1] with 50 grams of an amalgam, prepared by the addition of 2.5 grams of sodium to 500 grams of mercury, and 50 cc. of a like solution gave, in atoms, K : Na = 22.93 : 77.07.

(*c*) Fifty grams of electrolytically prepared lithium amalgam, containing 0.038 per cent of lithium, were treated for 30 minutes, at 17°, with 50 cc. of a like solution. A very feeble evolution of hydrogen took place.

The resulting amalgam gave, on analysis, KCl + NaCl = 0.0599 gram; K_2PtCl_6 = 0.0540 gram. The alcoholic filtrate from the potassium chlorplatinate was evaporated to dryness and the residue tested spectroscopically for lithium. None of that metal was present.

That is, the amalgam contained 0.0087 gram potassium and 0.0171 gram sodium; in atoms, K : Na = 23.05 : 76.95.

This ratio is a little below the mean (23.68 : 76.22) of those obtained with the sodium and potassium amalgams, where the small amounts of sodium and potassium leaving or entering

[1] *Loc. cit.*

the amalgams slightly altered the relative concentrations of sodium and potassium ions in the solutions employed. This source of error was eliminated by the use of lithium amalgam.

B. Rubidium and Sodium.

The Action of Rubidium and Sodium Amalgams on a Solution Containing Equimolecular Quantities of Sodium and Rubidium Chlorides.—The solution employed was made by dissolving a mixture of 11.70 grams of sodium chloride and 24.20 grams of rubidium chloride in water and diluting the solution to 100 cc.

(*a*) Fifty grams of rubidium amalgam were treated for 30 minutes, at 24°, with 50 cc. of the solution described above. In this case the evolution of hydrogen was very slow throughout the reaction, notwithstanding the presence of a trace of aluminium in the solution.[1]

The resulting amalgam gave, on analysis, RbCl + NaCl = 0.3839 gram; Rb_2PtCl_6 = 0.3596 gram.

That is, it contained 0.1063 gram rubidium and 0.0920 gram sodium; in atoms, Rb : Na = 23.75 : 76.25.

(*b*) Fifty grams of sodium amalgam were treated for 30 minutes, at 24°, with 50 cc. of the same solution. The evolution of hydrogen, which at first was very feeble, became more and more rapid, and, during the latter half of the action, very small bubbles of hydrogen were given off with such rapidity that the solution became milky white and opaque. The acceleration in the rate of evolution of hydrogen was caused by the presence of a trace of aluminium in the rubidium salt, which was of Merck's manufacture. This was, without doubt, due to its preparation from rubidium alum.

The resulting amalgam gave, on analysis, RbCl+NaCl = 0.0726 gram; Rb_2PtCl_6 = 0.0689 gram.

That is, it contained 0.02037 gram rubidium and 0.01726 gram sodium; in atoms, Rb : Na = 24.13 : 75.87.

C. Caesium and Sodium.

The Action of Caesium and Sodium Amalgams on a Solution Containing Equimolecular Quantities of Sodium and Caesium

[1] Cf. (*b*).

Chlorides.—The solution employed was made by dissolving a mixture of 5.85 grams of sodium chloride and 16.84 grams of caesium chloride in water and diluting the solution to 50 cc.

(*a*) Twenty-five grams of caesium amalgam were treated for 30 minutes, at 24°, with 25 cc. of the solution mentioned. The evolution of hydrogen was exceedingly feeble.

The resulting amalgam gave, on analysis, CsCl+NaCl = 0.0825 gram; Cs_2PtCl_6 = 0.0939 gram.

That is, it contained 0.03707 gram caesium and 0.01399 gram sodium; in atoms, Cs : Na = 32.95 : 67.05.

(*b*) Twenty-five grams of sodium amalgam were treated for 30 minutes, at 24°, with 25 cc. of the same solution. The evolution of hydrogen was even more feeble than it was with caesium amalgam and the same solution.

The resulting amalgam gave, on analysis, CsCl+NaCl = 0.1444 gram; Cs_2PtCl_6 = 0.1676 gram.

That is, it contained 0.06616 gram caesium and 0.02388 gram sodium; in atoms, Cs : Na = 32.44 : 67.55.

The results obtained in this series of experiments are very significant. They show clearly that the compounds of these metals with mercury are increasingly stable in the order: K, Rb, Cs, Na.

Summary.

Mercurial solutions of the hydrargyrides of sodium, potassium, rubidium, and caesium were subjected to the action of air, water, and aqueous ammonia, and finally each of the amalgams in the 3 pairs, Na and K, Na and Rb, and Na and Cs, was subjected to the action of the corresponding one of three equivalent solutions containing equimolecular quantities of sodium chloride and potassium, rubidium, or caesium chloride, and an equilibrium was attained in each case. From their behavior under these conditions, conclusions are drawn as to the relative stability of the alkali hydrargyrides.

Just as the hydrogen compounds of the halogens increase in stability with the increasing chemical activity of the halogens, so also the stability of the mercury compounds of calcium, strontium, and barium increases with the increasing chemical activity of the alkali earth metals. This is also true in the case

of potassium, rubidium, and caesium, the corresponding triad in the alkali group. The mercury compound of lithium is, by far, the least stable of the alkali hydrargyrides; and sodium, which forms the most stable hydrargyride in this group, behaves in this respect, as in many others, in an exceptional manner.

On exposure to a limited quantity of air, in closed vessels, the various amalgams are oxidized to different extents, and on the addition of water to the oxidized products oxygen is copiously evolved, with the simultaneous formation of hydrogen peroxide, in the cases of potassium, rubidium, and caesium; in the case of sodium, neither hydrogen peroxide nor oxygen is formed.

Like most of the other metals of the alkali and alkali earth groups the metals Cs–Na and Rb–Na are reversibly displaceable in aqueous solutions in the presence of mercury.

URBANA, ILL.,
May 17, 1907.

DISSOCIATION AS MEASURED BY FREEZING POINT LOWERING AND BY CONDUCTIVITY—BEARING ON THE HYDRATE THEORY. THE APPROXIMATE COMPOSITION OF THE HYDRATES FORMED BY A NUMBER OF ELECTROLYTES.

[NINETEENTH COMMUNICATION.]

BY HARRY C. JONES AND J. NEWTON PEARCE.

A brief summary of the evidence thus far obtained for the existence of hydrates in aqueous solutions of electrolytes is given below.

1. In the case of all electrolytes there exists between the water of crystallization and the temperature at which the crystals are formed a definite relation which, under the same conditions, is constant for a given salt. With increasing dilution the molecules and ions of an electrolyte are able to take up a part of the solvent, forming unstable molecular complexes or hydrates.

For equivalent concentrations the complexity of the hydrates formed by different salts stands in close relation to the amounts of water with which those salts crystallize from solution.

2. The abnormality in the freezing point lowerings produced by solutions of electrolytes is a function of the water of crystallization of these electrolytes. Those salts which have a greater number of molecules of water of crystallization always produce the greater lowering of the freezing point. The same relation has been found to hold for the molecular rise of the boiling point.

3. The minima in the boiling point and freezing point curves occur at those concentrations at which the effect of hydration just balances that produced by a decrease in the dissociation of the electrolyte. Owing to the instability of the hydrates formed with rise in temperature, the minima for the boiling point curves occur at greater concentrations than those for the freezing point curves.

4. The temperature coefficients of conductivity increase with increasing dilution. For salts which crystallize with the same amounts of water the temperature coefficients are of the same order of magnitude. Comparing salts which crystallize with different amounts of water, that one will have the largest temperature coefficient of conductivity which has the greatest power to combine with the solvent. In other words, the greater the power to bring water out of solution, as water of crystallization, the more complex will be the hydrate formed. The more complex the hydrate, the greater will be the temperature coefficient of conductivity.

5. The absorption bands produced by aqueous solutions of colored electrolytes widen with increase in concentration. The same effect is produced when an indifferent substance of strong dehydrating power is added. Similarly, increasing dilution, with its accompanying increasing hydration, decreases the width of the absorption bands.

Conductivity.

The conductivity of a solution of an electrolyte is a function of several conditions: the nature of the electrolyte

and the degree of its dissociation; the speed of its component ions; and the viscosity of the solvent. The degree of dissociation, in turn, depends upon the concentration of the electrolyte and the nature of the solvent.

As was pointed out by Dutoit and Aston, that solvent whose molecules are associated to the greatest extent has the greatest dissociating power.

Weak acids, weak bases, and salts of weak acids and bases show constantly increasing dissociation with increasing dilution, but, within the limits of accuracy of our present methods, no maximum of conductivity is directly obtainable. On the other hand, strong electrolytes show rapidly increasing dissociation with slight increase in dilution—a maximum conductivity being reached at moderate dilution.

It is stated by Ostwald[1] that the anions of the halogen acids move more rapidly than do those of the oxyhalogen acids, *e. g.*, $\overline{Cl}O_3$, $\overline{Br}O_3$, $\overline{I}O_3$; that $\overline{Cl}O_4$ has a greater migration velocity than IO_4. In general, the more complex the ion, the slower its migration velocity. Especially is this the case with the anions of organic acids. With isomeric anions, however, the velocities are approximately equal. With increasing increments of CH_2 the velocity decreases regularly. The same may be said with regard to the organic cations.

It has been proved by Jones and Getman and by Loomis[2] that organic acids are not hydrated. It is clear that increase in ionic volume is accompanied by decrease in ionic speed, doubtless due to increase in friction between ion and solvent.

With this idea in mind, and with the evidence from the freezing point measurements that the ions form more and more complex hydrates with increasing dilution, we are forced to believe that the conductivities of solutions of strong electrolytes are less than they would be, theoretically, if there were no hydration, by an amount which is a function of the volume of the ionic complex.

Vollmer[3] determined the values of λ_∞ for solutions of potas-

[1] Lehrbuch, **2**, 679.
[2] Wied. Ann., **60**, 523 (1897).
[3] *Ibid.*, Ann., **53**, 328 (1894).

sium acetate, sodium acetate, potassium iodide, lithium iodide, lithium chloride, and silver nitrate, in water and alcohol. He found the relation $\frac{\lambda'_\infty \ alc}{\lambda_\infty \ water} = K = 0.33$ to hold in every case.

Kawalki[1] found the same relation to exist between the speeds of diffusion of the same electrolytes in water and alcohol. It is of especial interest to note that the value which he obtained for his constant $\frac{D' alc}{D \ water} = K' = 0.33$ is the same as that found by Vollmer for conductivity. From their results we obtain the relation,

$$\lambda'_\infty : \lambda_\infty :: D' : D.$$

That this relation will hold, in case there is hydration or alcoholation, is highly probable, since the resistance offered to the ionic complex will be the same in each case.

As stated by Jahn,[2] "recent measurements have made it probable that the mobility of the ions is not independent of their concentration, that they have greater mobility in more concentrated than in more dilute solutions." Reference to the work of Jones and Bassett[3] shows that this is just what we should expect. They found, by freezing point measurements, that the hydration per gram molecule of the electrolyte decreases, with increasing concentration, to a certain concentration corresponding to the minimum in the molecular lowering of the freezing point, and then decreases very slowly with increasing concentration. In the more concentrated solutions, then, we have smaller changes in hydration; therefore, smaller changes in the ionic volumes; hence, we should have smaller changes in the mobility of the ions.

That the conductivity depends, in no small degree, upon the viscosity of the solution has been known for a long time, yet the simultaneous action of the two conditions, dissociation and viscosity, renders it impossible to separate their effects. No simple relation exists other than that the conductivity decreases with increase in viscosity.

[1] Wied. Ann., **52**, 300 (1894).
[2] Grundriss der Electrochemie, p. 143.
[3] This Journal, **33**, 534 (1905).

G. Wiedemann[1] first called attention to the fact that the friction which the ions produce in their motion changes in the sense that the fluidity changes. Accordingly, the mobility of the ions should be a function of the fluidity of the solution.

That the conductivity does not depend exclusively upon the fluidity can be seen in the following case: A 1 per cent (by volume) solution of cane sugar and a 2.2 per cent solution of methyl alcohol have the same internal friction, *viz.*, 1.046, but the conductivity of potassium chloride in a 1 per cent sugar solution is decreased 3 per cent, while in 2.2 per cent methyl alcohol it is decreased 3.85 per cent.

Pissarjewski and Lemcke[2] made the simple assumption that the conductivity is directly proportional to the dissociation, and inversely proportional to the viscosity, *e. g.*, $\mu = K\frac{\alpha}{\eta}$. At maximum disociation $K = \mu_\infty \eta_\infty$. Therefore, the dissociation is $\alpha' = \frac{\mu_v \eta_v}{\mu_\infty \eta_\infty}$ and not $\alpha = \frac{\mu_v}{\mu_\infty}$.

In the dilutions which they used the K, calculated from $\alpha = \frac{\mu_v}{\mu_\infty}$, varies, while K, calculated from $\alpha = \frac{\mu_v \eta_v}{\mu_\infty \eta_\infty}$, is a constant.

The Object of This Investigation.

It was our plan in this work to study the relation between the dissociation as measured by the freezing point and conductivity methods; to determine to just what extent the conductivity of a solution is influenced by the hydration of the ions; and to study the effect of hydration upon the relative velocities of different ions.

Moreover, it was desired to test the reliability of the conductivity method as a means of measuring the dissociation of strong electrolytes.

In order to do this, it was found necessary to redetermine as accurately as possible the freezing point lowerings produced by various solutions of a large number of salts.

[1] Pogg. Ann., **99**, 228 (1856).
[2] Z. physik. Chem., **52**, 479 (1905).

The object of the conductivity measurements was to determine the dissociation of the solution in question, as accurately as possible, in order that the theoretical lowering produced by the substance, if there was no hydration, might be calculated.

The freezing point measurements give us, on the other hand, an exact proportion between the number of dissolved particles, molecules, ions, or the hydrates of these, and the number of molecules of the solvent acting as such.

EXPERIMENTAL.

Freezing Point Apparatus.—For all concentrations from the most dilute up to those which could not be frozen by mixtures of salt and ice, a bath of rather large dimensions was used. The outer cylindrical vessel was made of heavy galvanized iron—diameter 31 cm., depth 26 cm.—and covered on the outside by a heavy coat of felt to prevent radiation. Within this was a much smaller vessel of the same material with a tightly fitting cover. Soldered around the large hole in the center of the cover is a conical-shaped collar, which holds firmly the cork through which the thermometer is inserted. By this means the thermometer always reaches to the same depth in the solution. A second smaller hole in the side is provided for the passage of the stirrer. To the bottom and on the outside was soldered a short bolt, which, in turn, was screwed into a nut soldered to the center of the outer vessel. In this way firm support was given the inner vessel and danger of floating was avoided. The freezing tube proper was a large glass tube—length 17 cm., diameter 5.5 cm., and of 250 cc. capacity. It was supported within the smaller vessel at the bottom by a cork, and at the top by a cork ring which rested upon an iron ledge soldered to the inside of the small vessel. These dimensions allowed for an air space of about 2 cm. all around.

The stirrer consisted of a gold-plated brass disc with one large hole in the center to permit the passage of the thermometer, and around this smaller holes about 0.7 cm. in diameter.

Near the top of the large outer cylinder was soldered a small tube which served to keep the water in the bath at constant level.

By means of a bath of these dimensions the temperature of the freezing mixture could be kept constant for five or six hours. No attempt was made to control exactly the temperature of the bath, but experience taught us that only those freezing mixtures which required from forty seconds to one minute to cool the solution 0°.1 could be depended upon for reliable results.

For solutions requiring freezing mixtures of calcium chloride, and in the ordinary cryoscopic apparatus consisting of a battery jar, two test tubes were used.

For this work 4 thermometers of the Beckmann type were employed, whose temperature ranges were 1°.1, 5°.6, 12°.2, and 25°. These were graduated into 0°.002, 0°.01, 0°.02, and 0°.05, respectively (whole scale). By means of a high-power lens it was easy to read to a tenth of the above graduations.

Conductivity.

Apparatus.—The conductivity measurements were made by means of the well-known Kohlrausch method, using the Wheatstone bridge, induction coil, and telephone receiver. The wire was calibrated according to the method of Strouhal and Barus.[1] The resistance coils were made by Leeds, of Philadelphia, and had been carefully calibrated.

Conductivity cells of two types were used. For the more dilute solutions cells of the type devised by Jones and Bingham[2] were employed. For the more concentrated solutions U-shaped cells, similar to those used by Jones and Getman,[3] were found to be very convenient.

All conductivity measurements were made at 0°. For this purpose a small pail was filled with finely crushed ice, moistened with distilled water, and the cells packed into the ice as tightly as possible. The small pail was then placed

[1] Wied. Ann., **10**, 326 (1880).
[2] This Journal, **34**, 481 (1905).
[3] Z. physik. Chem., **48**, 244 (1903).

in a spacious pan and the space between the pail and the pan filled with finely crushed ice.

Specific Gravity.

Since the solutions were made up at 20°, we thought it best to determine their specific gravities at the same temperature. The 20° bath was a large galvanized iron tub. By means of a very small flame below and a stirrer within, driven by a hot-air motor, the temperature could easily be kept to within 0°.1 of the desired temperature. Throughout this work six pycnometers of the Ostwald type were employed. They were carefully calibrated with pure redistilled water.

Volumetric Apparatus.

The flasks and burettes used in this work were carefully calibrated at 20° by the method of Morse and Blalock.[1]

Solutions.

Kahlbaum's "chemically pure" materials were used in every case and were further purified whenever it was thought desirable to do so. The method of preparing the solutions varied according to the solute employed. In general, a solution of slightly greater concentration than 2 normal was first made, and from this, by successive dilutions, the lesser concentrations were obtained. Whenever possible, the mother solution was made up by direct weighing; when the nature of the solute did not permit it to be weighed, the mother solution was diluted to convenient strength, and portions of the dilute solution were standardized either by gravimetric or volumetric methods.

Water.

The water which was used in all the solutions was purified according to the method of Jones and Mackay.[2] Ordinary distilled water was twice redistilled from an acidified solution of potassium dichromate, and the steam from the second distillation passed through a boiling solution of barium

[1] THIS JOURNAL, **16**, 479 (1894).
[2] *Ibid.*, **19**, 83 (1897).

hydroxide. It had, at 0°, a conductivity of about 1.2×10^{-6} to 1.7×10^{-7}.

Calculation of the Composition of the Hydrates.

The method of calculating the amount of water combined with the dissolved substance is essentially the same as that used by Jones and Bassett.[1] We have given the observed molecular lowering of the freezing point, the specific gravity of the solutions, and the dissociation. The observed molecular lowering is corrected for the difference between 1000 grams and the amount of water actually present in one liter of the solution. This gives the true molecular lowering which would be produced by the substance at the dilution in question if there were 1000 grams of water present.

From the dissociation we calculate the true molecular lowering which would be produced by the dissolved substance if there were no hydration; and if there is no hydration these two values for the molecular lowering should be equal.

The calculated lowering, divided by the observed lowering and multiplied by 1000, gives the amount of water present playing the rôle of solvent, if the quantity of the substance present is dissolved in 1000 grams of water.

The difference between this amount of water and 1000 grams gives the amount of water which is combined with the dissolved substance in the solution in question.

Knowing the number of grams of water which are in combination with the dissolved substance, the number of gram molecules of water combined with the substance is obtained by dividing this number by 18. If we divide this value by the concentration in terms of normal, we obtain the number of molecules of water which are in combination with one molecule of the dissolved substance when the amount of substance present in one liter of the solution is dissolved in 1000 grams of water.

In the various tables of data the symbols have the following significance:

In the tables of freezing point measurements m is the con-

[1] This Journal, **33**, 843 (1905); **34**, 298 (1905).

centration in terms of gram molecules per liter; Δ, the observed lowering of the freezing point, corrected for the separation of ice; Δ/m, the molecular lowering of the freezing point.

In the conductivity tables, V denotes the volume of the solution in liters which contains one gram molecular weight of the electrolyte; μ is the conductivity corrected for water; α is the approximate dissociation.

In the specific gravity tables, m is the concentration; W_{sol}, the weight of one liter of the solution; W_{salt} is the weight of the salt contained in one liter of the solution; and W_{H_2O} is the weight of water contained in one liter of the solution. The percentage correction is the correction which must be applied to the freezing point lowering in order to refer it to 1000 grams of the solvent instead of the amount of water that is actually present in one liter of the solution in question.

In the hydrate tables, m is the concentration in gram molecules per liter; α, the approximate dissociation as measured by the conductivity method; L, the theoretical molecular lowering of the freezing point referred to 1000 grams of solvent; Δ/m, the observed molecular lowering; L', the corrected molecular lowering; M, the number of gram molecules of water in combination with the solute; and H, the number of gram molecules of water combined with one molecule of the salt at the concentration in question.

Calcium Chloride.

The data for calcium chloride are given in Tables I. to IV. The value of μ_∞ is surprisingly low, when compared with that obtained by West[1] and by Bassett.[2] It is, however, very nearly equal to that obtained by Jones and Stine.[3]

A study of Table IV. leads us to the following conclusions: The theoretical molecular lowerings, as given in column L, decrease regularly with increase in concentration, while the corrected observed molecular lowerings, as seen in column L',

[1] THIS JOURNAL, **34**, 393 (1905).

[2] *Ibid.*, **33**, 547 (1905).

[3] The article of Jones and Stine will be published in THIS JOURNAL in the near future.

decrease rapidly, reach a minimum at 0.1 normal, and then increase with increase in concentration.

It is very probable that the value of L' for 0.01 normal is too large, but owing to the inaccuracy of the method for such dilutions, this is unavoidable.

It will be seen from column M that the amount of water which has entered into combination with the dissolved salt also passes through a minimum between 0.075 normal and 0.10 normal—the same concentration which gives the minimum molecular lowering of the freezing point. A similar minimum was noted by Jones and Bassett[1] for concentrations ranging from 0.102 normal to 0.153 normal. It has been assumed hitherto, by Jones and his coworkers, that the minimum in the freezing point lowering always occurs in that concentration where the effect due to decrease in dissociation is just counterbalanced by the effect due to hydration. The values of L' and M also show that the abnormality of the freezing point lowering is greatly augmented by the relatively great hydrating power of the ions, since it is the ions with which we are chiefly concerned in the dilute solutions. A glance at column H shows us at once the great hydrating power of the ions in dilute solution. The values of H decrease regularly with increase in concentration to 0.10 normal. From that concentration on, the decrease in hydration is very slight as the concentration increases. In these concentrations the combined effect upon the freezing point lowering, due both to the dissociation and to the hydration of the ions, is small, compared with the effect due to the undissociated molecules.

If we refer to the literature[2] bearing upon the relation between the water of crystallization of a salt and the temperature at which it crystallizes, we see that, over a definite range of temperature, the amount of water of crystallization is constant. If, then, we eliminate the hydration due to the ions, we should expect to find the number of molecules of water combined with one molecule of the salt to be a constant for

[1] This Journal, **33**, 548 (1905).
[2] Bassett: This Journal, **34**, 294 (1905).

a definite range of temperature. This is clearly shown by the values of H for the more concentrated solutions.

The values of M are plotted in the curve (Fig. II.) against the concentrations as abscissas. The curve shows, at a glance, that the amount of water held in combination, from the dilution at which the minimum occurs, is a linear function of the concentration.

The values of H are plotted in the curve (Fig. I.) against the concentrations as abscissas. An explanation regarding

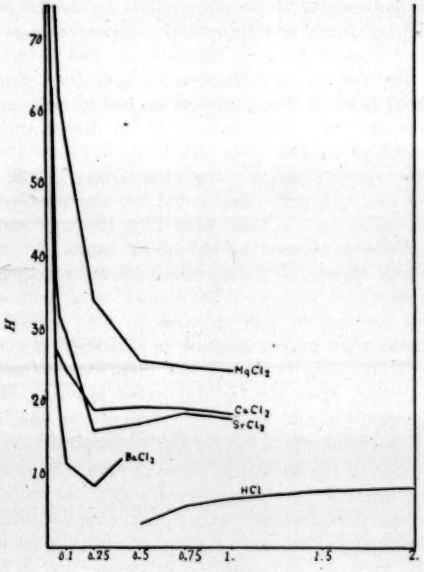


Fig. I.

these hydrate curves is necessary at this point. With one or two exceptions, it was found impossible to plot on the paper the values of H for the more dilute solutions.

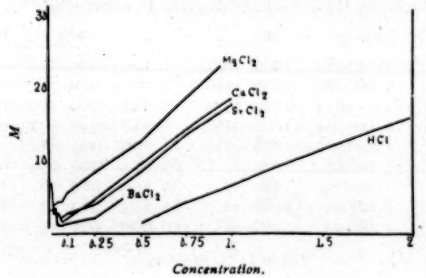


Fig. II.

These curves show the rapid decrease in hydration until the minimum is reached, and then a very slight decrease with increasing concentration.

Table I.—Freezing Point Measurements.

m.	Δ.	Δ/*m.*	*i.*	*α.*
0.01	0.05945	5.9450	.....	.....
0.025	0.1318	5.2720	2.8344	91.72
0.05	0.2511	5.0220	2.7000	85.00
0.075	0.3651	4.8690	2.6177	80.88
0.10	0.48515	4.8515	2.6083	80.41
0.25	1.2335	4.9340	2.6526	
0.50	2.6270	5.2540	2.8247	
0.75	4.1955	5.5940	3.0075	
1.00	6.1040	6.1040	3.2817	

Table II.—Conductivity Measurements.

μ_∞ 0° = 123.46.

V.	μ_v.	*α.*
100	111.23	89.67
40	104.66	84.37
20	100.01	80.62
13.34	95.02	76.60
10	92.23	74.35
4	87.19	70.62
2	80.73	65.39
1.334	74.69	60.49
1.00	70.98	57.49

Table III.—Specific Gravity Measurements.

m.	Sp. gr.	$W_{sol.}$	W_{salt}.	W_{H_2O}.	Per cent of correction.
0.01	1.000982	1000.982	1.109	999.873	0.012
0.025	1.002539	1002.539	2.772	999.767	0.023
0.05	1.004874	1004.874	5.545	999.329	0.067
0.075	1.006814	1006.814	8.317	998.497	0.150
0.10	1.008971	1008.971	11.090	997.881	0.211
0.25	1.02267	1022.67	27.725	994.954	0.504
0.50	1.04451	1044.51	55.450	989.06	1.094
0.75	1.06641	1066.41	83.175	983.23	1.676
1.00	1.08744	1087.44	110.900	976.54	2.345

Table IV.—Hydrates.

m.	*a.*	*L.*	Δ/m.	*L'.*	*M.*	*H.*
0.025	84.37	4.9885	5.2720	5.2708	2.869	114.7
0.05	80.62	4.7590	5.0220	5.0187	2.874	57.4
0.075	76.60	4.7095	4.8690	4.8617	1.742	23.2
0.10	74.35	4.6258	4.8515	4.8414	2.474	24.7
0.25	70.62	4.487	4.934	4.910	4.785	19.1
0.5	65.39	4.293	5.254	5.197	9.663	19.3
0.75	60.49	4.110	5.594	5.501	14.048	18.7
1.00	57.49	3.998	6.104	5.962	18.30	18.3

Strontium Chloride.

The concentrated mother solution was diluted to convenient strength and equal portions were taken for standardization. The strontium was precipitated and weighed as strontium carbonate.

The conductivity measurements for this salt gave us, at maximum dissociation, $\mu_\infty = 128.57$. The corresponding value obtained by Jones and Stine[1] was $\mu_\infty = 128.44$.

The minimum in the freezing point lowerings (column L') is found at 0.25 normal, whereas the minimum in the total combined water occurs at a somewhat greater dilution (0.05 normal). The values of H become approximately constant at 0.25 normal, the minimum point in the freezing point lowering.

The values of m and H for calcium and strontium chlorides, Tables IV. and VIII., show numbers of approximately the same order of magnitude. For curves, see Figs. I. and II.

[1] *Loc. cit.*

Table V.—Freezing Point Measurements.

m.	Δ.	Δ/m.	i.	α.
0.01	0.05273	5.2730	2.8351	91.87
0.02937	0.1550	5.2800	2.8386	91.93
0.03987	0.2026	5.0752	2.7382	86.91
0.5011	0.2476	4.9349	2.6531	82.65
0.7077	0.3472	4.9060	2.6376	81.88
0.10	0.48904	4.8904	2.6292	81.46
0.25	1.1957	4.7830	2.5715	78.57
0.50	2.5339	5.0678	2.7354	.....
0.75	4.0989	5.4652	2.9385	.....
1.00	5.9211	5.9211	3.1833	.....

Table VI.—Conductivity Measurements.

μ_∞ 0° = 128.57 (Stine 128.4).

V.	μ_v.	α.
1100	128.57	.....
550	127.99	.....
100	115.64	89.37
34.04	106.10	82.56
25.08	103.26	80.32
19.93	101.04	78.08
14.03	98.06	76.27
10	95.98	74.17
4	88.07	68.59
2	82.18	63.96
1.333	74.86	58.30
1.0	71.23	55.47

Table VII.—Specific Gravity Measurements.

m.	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent of correction.
0.01	1.0012284	1001.2284	1.585	999.7034	0.029
0.02937	1.0038396	1003.8396	4.6559	999.2837	0.071
0.03987	1.0053832	1005.3832	6.3197	999.0635	0.093
0.05017	1.007028	1007.028	7.952	999.078	0.092
0.07077	1.00956	1009.516	11.217	998.299	0.170
0.10	1.013205	1013.215	15.85	997.930	0.207
0.25	1.034433	1034.433	38.625	994.808	0.519
0.5	1.068379	1068.379	79.250	989.129	1.087
0.75	1.101760	1101.160	118.875	982.885	1.711
1.00	1.135423	1135.423	158.50	976.923	2.308

Table VIII.—Hydrates.

m.	*α.*	*L.*	*Δ/m.*	*L′.*	*M.*	*H.*
0.01	89.37	5.1845	5.2733	5.2718	.....	.....
0.02937	82.56	4.9312	5.2800	5.2763	3.634	123.6
0.03987	80.32	4.8479	5.0752	5.0705	2.439	61.2
0.05017	78.08	4.7645	4.9349	4.9304	1.871	37.2
0.07077	76.27	4.6982	4.9060	4.8977	2.274	32.13
0.10	74.17	4.6191	4.8904	4.8803	2.973	29.73
0.25	68.59	4.4115	4.7830	4.7582	4.047	16.18
0.50	63.96	4.2393	5.0678	5.0127	8.572	17.14
0.75	58.30	4.0287	5.4652	5.3718	13.890	18.52
1.00	55.47	3.9234	5.9211	5.7844	17.873	17.87

As in the case of calcium chloride, the values of the theoretical lowerings (L) are less than the observed lowerings (L') in every instance.

Magnesium Chloride.

The value of μ_∞ for magnesium chloride was found to be 123.95. The values of L' show a minimum at 0.25 normal, while the values of H begin to be constant at 0.5 normal. Magnesium chloride differs from the other chlorides thus far discussed in that its values for M show no minimum, but increase regularly with increasing concentration.

It should be noticed also that magnesium chloride has greater power to combine with water than any of the halides of the calcium group. Especially is this the case in the dilute solutions, where the ions predominate. That this is not due to hydrolysis and the liberation of the free mineral acid is evident from the fact that the molecular lowering of the freezing point in the dilute solutions is in every case considerably higher than the calculated lowering. As we shall see later, in our study of the acids just the reverse was found to be the case. The curves for this salt are found in Figs. I. and II.

Table IX.—Freezing Point Measurements.

m.	Δ.	Δ/*m.*	*i.*	*α.*
0.004928	0.02741	5.5630	2.9909	99.54
0.007317	0.04072	5.5643	2.9916	99.58
0.01	0.05472	5.4720	2.9420	97.10
0.05108	0.2678	5.2443	2.8195	90.75
0.07171	0.3687	5.1421	2.7651	88.25
0.09986	0.5133	5.1330	2.7596	87.68
0.25	1.2352	4.9408	2.6563	82.81
0.50	2.6768	5.3536	2.8783	
0.75	4.4328	5.9104	3.1776	
0.9415	6.0619	6.4885	3.4615	

Table X.—Conductivity Measurements.

μ_∞ 0° = 123.95.

V.	μ_v.	*α.*
402.25	120.15	96.94
202.92	116.67	94.13
136.67	113.86	91.86
100.0	112.68	90.90
32.21	103.08	83.16
19.57	98.88	79.78
13.94	95.36	76.93
10.0	91.25	73.61
4.0	80.22	64.72
2.0	72.07	59.50
1.333	64.69	53.63
1.062	60.31	48.66

Table XI.—Specific Gravity Measurements.

m.	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent of correction.
0.00493	1.000344	1000.344	0.4695	999.875	0.012
0.007327	1.000524	1000.524	0.6970	999.827	0.017
0.01	1.000842	1000.842	0.9526	999.889	0.012
0.03104	1.002756	1002.756	2.9568	999.799	0.020
0.05108	1.004224	1004.224	4.9168	999.307	0.069
0.07171	1.006036	1006.036	6.8316	999.204	0.079
0.100	1.008505	1008.505	9.5260	998.979	0.102
0.25	1.020966	1020.966	23.8150	997.151	0.284
0.50	1.038496	1038.496	47.630	990.866	0.910
0.75	1.056905	1056.905	71.445	985.460	1.450
0.9415	1.069617	1069.617	89.689	979.930	2.007

Table XII.—Hydrates.

m.	*α.*	*L.*	*Δ/m.*	*L′.*	*M.*	*H.*
0.01	90.90	5.2415	5.4720	5.4714	2.334	233.4
0.03104	83.16	4.9535	5.3581	5.3570	4.185	134.82
0.05108	79.78	4.8278	5.2443	5.2407	4.377	85.69
0.07171	76.93	4.7218	5.1421	5.1381	4.501	62.76
0.10	73.61	4.5982	5.1330	5.1278	5.737	57.37
0.25	64.72	4.1675	4.9408	4.9268	8.562	34.24
0.50	59.50	4.0734	5.3536	5.3049	12.898	25.79
0.75	53.63	3.8550	5.9104	5.8247	18.787	25.05
0.9415	48.66	3.6701	6.4385	6.3098	23.242	24.68

Barium Chloride.

A nearly saturated solution of this salt was first made. This was diluted to convenient concentration, and equal portions were precipitated and weighed as barium sulphate. Owing to the slight solubility of this salt, we did not attempt to work with concentrations greater than 0.4 normal.

Conductivity measurements gave us the value $\mu_\infty = 132.07$.

Table XIII.—Freezing Point Measurements.

m.	*Δ.*	*Δ/m.*	*i.*	*α.*
0.01	0.5463	5.4630	2.9370	96.85
0.025	1.3398	5.3592	2.8813	94.06
0.05	0.24770	4.9551	2.6639	83.19
0.075	0.36128	4.8171	2.5898	79.49
0.10	0.4792	4.7925	2.5766	78.83
0.25	1.1669	4.6677	2.5095	75.47
0.40	1.902	4.7370	2.5575	

Table XIV.—Conductivity Measurements.

μ_∞ 0° = 132.07.

V.	μ_v.	*α.*
100	120.01	90.87
40	111.15	84.16
20	105.78	80.09
13.33	100.69	76.24
10	99.92	75.65
4	92.18	69.79
2.5	86.31	65.35

Table XV.—Specific Gravity Measurements.

m.	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent of correction.
0.01	1.001878	1001.87	2.083	999.795	0.021
0.025	1.00475	1004.75	5.207	999.545	0.045
0.05	1.00929	1009.29	10.415	998.879	0.112
0.75	1.01369	1013.69	15.622	998.074	0.197
0.10	1.01766	1017.66	20.830	996.83	0.316
0.25	1.0456	1045.61	52.075	993.542	0.645
0.40	1.0726	1072.65	83.32	989.335	1.066

Table XVI.—Hydrates.

m.	*a.*	*L.*	$\Delta/m.$	*L'.*	*M.*	*H.*
0.025	84.16	4.9907	5.3592	5.3568	3.796	151.8
0.05	80.09	4.8393	4.9551	4.9496	1.238	24.7
0.075	76.24	4.6961	4.8171	4.8080	1.293	17.2
0.10	75.65	4.6742	4.7925	4.7772	1.197	11.9
0.25	69.79	4.4562	4.6677	4.6374	2.172	8.69
0.40	65.35	4.2910	4.7570	4.7061	4.900	12.25

What has been said regarding the chlorides of calcium, strontium, and magnesium applies equally well to barium chloride. The low value of H for 0.25 normal is doubtless due to experimental error.

It is interesting to note that while the molecules of barium chloride have a much smaller hydrating power than the other chlorides of the alkaline earth metals, as we should expect from the fact that it crystallizes with but two molecules of water, the ions which predominate in the dilute solutions have a relatively high hydrating power.

Another point is to be noted, one to which reference will be made later in this paper. A glance at the curves representing the values of M and H for the three salts—calcium, strontium, and magnesium chlorides—will show that in each case the curves for calcium chloride lie above those for strontium chloride, while the two curves for magnesium chloride lie above those for calcium chloride. *This order is just the reverse of that for the atomic volumes of the three metals.* Although barium chloride crystallizes with but two molecules of water, the atomic volume of barium is still larger than that of strontium. This may account for the relatively high hydrating power of the ions of barium salts.

The curves for the values of M and H are given in Figs. II. and I., respectively.

Calcium Nitrate.

The mother solution was diluted and 50 cc. portions were taken for standardization. The calcium was precipitated by means of ammonium oxalate and weighed as calcium oxide. The data are given in Tables XVII. to XX.; the curves are plotted in Figs. III. and IV.

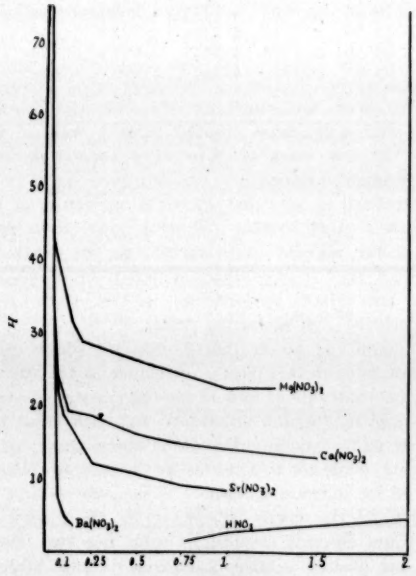


Fig. III.

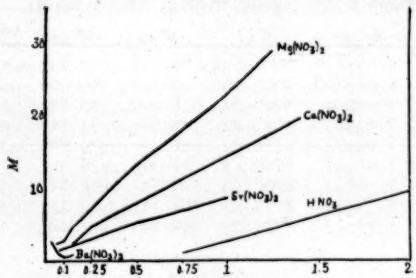


Fig. IV.

Table XVII.—Freezing Point Measurements.

m.	Δ.	Δ/*m.*	*i.*	*α.*
0.0125	0.072	5.7560	.....	.....
0.025	0.1303	5.2120	2.8021	90.10
0.05	0.2405	4.8090	2.5855	79.27
0.125	0.5752	4.6019	2.4736	73.68
0.25	1.1424	4.5695	2.4567	72.83
0.5	2.2860	4.5720	2.4580	
0.75	3.484	4.645	2.4974	
1.0	4.766	4.766	2.5623	
1.5	7.616	5.077	2.7299	

Table XVIII.—Conductivity Measurements.

μ_∞ 0° = 126.69.

V.	μ_v.	*α.*
0.80	108.60	85.72
0.40	102.78	81.13
0.20	96.28	76.00
8.0	85.72	67.66
4.0	77.64	61.28
2.0	66.54	52.52
1.333	58.32	46.03
1.0	51.30	40.49
0.6667	40.24	31.75

Table XIX.—Specific Gravity Measurements.

m.	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent of correction.
0.0125	1.001846	1001.846	2.052	999.794	0.021
0.025	1.003166	1003.166	4.104	999.062	0.094
0.05	1.00604	1006.04	8.209	997.831	0.217
0.125	1.01523	1015.23	20.520	994.71	0.529
0.25	1.03074	1030.74	41.04	989.70	1.03
0.5	1.06011	1060.11	82.09	978.02	2.198
0.75	1.08874	1008.74	123.13	965.61	3.439
1.00	1.11751	1117.51	164.18	953.33	4.66
1.5	1.17375	1173.75	246.27	927.48	7.25

Table XX.—Hydrates.

m.	*a.*	*L.*	$\Delta/m.$	*L'.*	*M.*	*H.*
0.025	81.13	4.8780	5.2120	5.2072	3.511	140.4
0.05	76.00	4.6872	4.8090	4.7986	1.288	25.7
0.125	67.66	4.3769	4.6019	4.5776	2.437	19.5
0.25	61.28	4.139	4.569	4.522	4.703	18.8
0.5	52.52	3.813	4.572	4.471	8.173	16.3
0.75	46.03	3.572	4.645	4.485	11.312	15.07
1.00	40.49	3.366	4.766	4.544	14.490	14.49
1.5	31.75	3.041	5.077	4.709	19.683	13.12

Nothing special need be said regarding the data for this salt, except to call attention to the fact that the amounts of water combined with calcium chloride in solution are, in general, higher than the amounts combined with calcium nitrate. This is just what we should expect when we consider that calcium chloride crystallizes with 6 molecules of water, while calcium nitrate crystallizes with 4.

Strontium Nitrate.

The strontium was precipitated and weighed as the carbonate. Unlike the other salts thus far studied, the freezing point lowerings show no minimum within the range of concentrations used, the molecular lowering constantly decreasing in value. A minimum was, however, obtained by Jones and Bassett[1] at a concentration of about 1.5 normal.

[1] THIS JOURNAL, **34**, 305 (1905).

Table XXI.—Freezing Point Measurements.

m.	Δ.	Δ/*m.*	*i.*	*α.*
0.01	0.05717	5.7170	3.0736	103.68
0.025	0.1304	5.2180	2.8053	90.27
0.05	0.2402	4.8050	2.5833	79.16
0.075	0.3492	4.6567	2.5036	75.18
0.10	0.4587	4.5875	2.4664	73.32
0.25	1.0817	4.326	2.3263	66.31
0.5	2.0849	4.169	2.2418	62.09
0.75	3.0453	4.060	2.1829	59.15
1.00	3.9983	3.9983	2.1496	57.48

Table XXII.—Conductivity Measurements.

μ_∞ 0° = 125.62.

V.	μ_v.	*α.*
100	111.14	88.47
40	100.95	80.36
20	94.12	74.92
13.34	89.26	71.06
10	86.16	68.59
4	73.59	58.58
2	61.34	48.83
1.33	52.77	42.01
1	45.69	36.37

Table XXIII.—Specific Gravity Measurements.

m.	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent of correction.
0.01	1.001525	1001.525	2.116	999.409	0.059
0.025	1.004207	1004.207	5.292	998.915	0.108
0.05	1.008391	1008.391	10.584	997.807	0.219
0.075	1.012646	1012.646	15.876	996.77	0.323
0.10	1.016834	1016.834	21.168	995.666	0.433
0.25	1.04201	1042.01	52.92	989.09	1.09
0.5	1.08312	1088.12	105.84	977.28	2.27
0.75	1.12386	1123.86	158.76	965.11	3.48
1.00	1.16354	1163.54	211.68	951.86	4.814

Table XXIV.—Hydrates.

m.	*α.*	*L.*	*Δ/m.*	*L′.*	*M.*	*H.*
0.025	80.36	4.8493	5.7180	5.7124	3.870	154.8
0.05	74.92	4.6470	4.8050	4.7945	1.710	34.20
0.075	71.06	4.5034	4.6567	4.6418	1.657	22.09
0.10	68.59	4.4115	4.5875	4.5677	1.900	19.00
0.25	58.58	4.0391	4.3269	4.2798	3.124	12.49
0.5	48.83	3.676	4.169	4.075	5.437	10.87
0.75	42.01	3.422	4.060	3.918	7.030	9.37
1.00	36.37	3.213	3.998	3.806	8.607	8.65

The values for the combined water show a minimum at 0.075 normal, just as calcium nitrate does.

The hydration per ion and molecule also shows no tendency to become constant.

The curves are plotted in Figs. III. and IV.

Magnesium Nitrate.

The nitrate of magnesium, like the chloride, shows a much greater power to combine with water, throughout the range of concentration studied, than do the nitrates of the alkali earth metals.

Table XXV.—Freezing Point Measurements.

m.	*Δ.*	*Δ/m.*	*i.*	*α.*
0.02	0.1078	5.3903	2.8980	94.90
0.05	0.24968	4.9938	2.6848	84.24
0.10	0.49085	4.9085	2.6390	81.95
0.15	0.74486	4.9671	2.6705	83.52
0.20	0.99875	4.9937	2.6848	
0.50	2.74280	5.4856	2.9492	
1.00	6.5145	6.5145	3.5024	

Table XXVI.—Conductivity Measurements.

μ_∞ 0° = 119.90.

V.	μ_v.	*α.*
50	102.06	85.12
20	94.48	78.80
10	89.66	74.78
6.666	85.61	71.40
5	83.04	69.25
2	72.03	60.07
1	59.27	49.43

Table XXVII.—Specific Gravity Measurements.

m.	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent of correction.
0.02	1.00224	1002.224	2.968	999.255	0.074
0.05	1.005626	1005.626	7.422	998.204	0.179
0.10	1.011118	1011.118	14.844	996.274	0.372
0.15	1.016557	1016.557	22.266	994.291	0.571
0.20	1.022026	1022.026	29.688	992.338	0.766
0.50	1.054804	1054.804	74.220	980.584	1.941
1.00	1.107865	1107.865	148.440	959.425	4.057
1.274	1.136615	1136.615	189.112	947.502	5.249

Table XXVIII. Hydrates.

m.	*a.*	*L.*	$\Delta/m.$	*L'.*	*M.*	*H.*
0.05	78.80	4.7913	4.9938	4.9849	2.157	43.14
0.10	74.78	4.6418	4.9085	4.8903	2.817	28.17
0.15	71.40	4.5161	4.9671	4.9388	4.759	31.73
0.20	69.25	4.4361	4.9937	4.9555	5.819	29.09
0.50	60.07	4.0946	5.4856	5.3792	13.260	26.52
1.00	49.43	3.6988	6.5145	6.2507	22.672	22.67
1.274	44.46	3.5139	7.1032	6.7303	29.006	22.76

The amount of water decreases with increase in concentration in the dilute solutions, reaches a minimum at 0.05 to 0.075 normal, and then increases regularly with increase in concentration.

The values of *H* do not approach a constant until normal concentration is reached.

It is very probable that the relatively low values of *H* for 0.05 and 0.1 normal are due to errors in measuring the freezing points of those solutions.

The curves for magnesium nitrate are given in Figs. III. and IV.

Barium Nitrate.

Owing to the very small solubility of this salt we did not attempt to make measurements beyond 0.15 normal. Barium nitrate has special interest in that it is the first salt thus far studied in this investigation which, under ordinary conditions, crystallizes without water.

Table XXIX.—Freezing Point Measurements.

m.	Δ.	Δ/m.	i.	α.
0.01	0.05545	5.5450	2.9812	99.06
0.025	0.12482	4.9928	2.6838	84.19
0.05	0.23281	4.6566	2.5035	75.18
0.075	0.32704	4.3606	2.3440	67.20
0.10	0.42018	4.2018	2.2590	62.95
0.15	0.59935	3.9955	2.1481	57.40

Table XXX.—Conductivity Measurements.

μ_∞ 0° = 128.08.

V.	μ_v.	α.
100	110.62	86.37
40	99.04	77.32
20	90.26	70.47
13.34	83.92	65.51
10	78.59	61.36
6.67	71.05	55.47

Table XXXI.—Specific Gravity Measurements.

m.	Sp. gr.	$W_{sol.}$	$W_{salt.}$	W_{H_2O}.	Per cent of correction.
0.01	1.002031	1002.031	2.14	999.891	0.088
0.025	1.005224	1005.224	6.537	998.687	0.131
0.05	1.010591	1010.591	13.074	997.517	0.248
0.075	1.015671	1015.671	19.611	996.060	0.394
0.10	1.021143	1021.143	26.148	994.995	0.500
0.15	1.031770	1031.770	39.222	992.548	0.745

Table XXXII.—Hydrates.

m.	α.	L.	Δ/m.	L'.	M.	H.
0.05	70.47	4.4814	4.6566	4.6451	1.957	39.15
0.075	65.51	4.2969	4.3606	4.3434	0.595	7.93
0.10	61.30	4.1425	4.2018	4.1808	0.509	5.09
0.10	55.47	3.9234	3.9955	3.9648	0.5805	3.87

It will be seen that, like strontium nitrate, the molecular lowering of the freezing point decreases regularly as the concentration increases, without showing a minimum value.

The amount of water held in combination decreases rapidly and reaches a minimum at 0.1 normal.

The hydration per molecule is very small, as we should expect, since the salt in its solid state is anhydrous. In the more dilute solutions, however, where the ions predominate, the hydration is of the same order as that of the other nitrates of the alkali earths.

This is, indeed, convincing proof that the ions themselves have great hydrating power.

It was pointed out in the introduction that if there were no hydration the corrected molecular lowering of the freezing point should be equal to the corrected lowering. A glance at Table XXXII. will show how closely the assumption agrees with facts. The values for the corrected freezing point lowerings for the three most concentrated solutions, in which the hydration is least, are only about one per cent higher than the calculated values. Moreover, if there is no hydration and if we may disregard the effect of viscosity upon the velocity of the ions, we should expect the dissociation as measured by the conductivity and freezing point methods to be the same. That this is true may be seen by consulting the values of α for 0.075, 0.10, and 0.25 normal in Tables XXIX. and XXX. Owing to slight hydration, the amounts of dissociation, as measured by the freezing point method, are slightly higher than those measured by the conductivity method.

The curves for barium nitrate are given in Figs. III. and IV.

Since the two barium salts studied are so slightly soluble, it was thought best to add the tables for the hydrates of barium bromide and barium iodide which were prepared by Jones and Bassett.[1] Both of these salts crystallize with two molecules of water of crystallization.

Table XXXIII.—Hydrates.

m.	α.	L.	Δ/m.	L'.	M.	H.
0.10	79.3	4.81	5.06	5.04	2.54	25.4
0.15	77.7	4.75	4.91	4.88	1.48	9.9
0.25	73.8	4.60	5.00	4.96	4.03	16.1
0.40	71.3	4.52	5.09	5.03	5.63	14.1
0.50	68.8	4.42	5.18	5.09	6.22	12.5
0.6774	65.3	4.29	5.74	5.59	12.92	19.1
0.9032	64.8	4.27	5.87	5.66	13.64	15.1
1.1290	61.1	4.13	6.24	5.93	16.88	14.9
1.3548	58.4	4.03	6.66	6.28	19.90	14.7
1.5806	55.6	3.93	7.12	6.63	22.66	14.3
1.884	50.90	3.75	7.67	7.06	26.05	14.4
2.258	41.1	3.39	8.343	7.58	30.71	13.6

[1] This Journal, **33**, 553 (1905); **34**, 306 (1905).

Table XXXIV.—Hydrates.

m.	*α.*	*L.*	*Δ/m.*	*L′.*	*M.*	*H.*
0.076	78.6	4.78	4.92	4.91	1.47	19.3
0.153	75.9	4.68	5.00	4.96	3.14	20.5
0.306	74.9	4.65	5.17	5.08	4.70	15.4
0.612	71.0	4.54	6.08	5.86	12.51	20.4
0.917	64.8	4.27	6.69	6.29	17.84	19.5
1.222	61.1	4.13	7.54	6.98	22.70	18.1
1.528	55.5	3.92	8.67	7.83	27.74	18.2
1.834	51.1	3.76	9.54	8.44	31.92	17.4
2.139	45.0	3.53	11.22	9.67	35.28	16.5

The solubilities of these two salts are nearly equal to that of the other halides of the calcium group. It is very probable, owing to the fact that Jones and Bassett used a thermometer less sensitive than the one employed in this work, that the observed freezing point lowerings for the most dilute solutions are too low. This would, of necessity, give low values for the total combined water and for the hydration

The values of *M* for these salts increases regularly with increase in concentration. The magnitude of hydration for each salt is approximately constant. If we compare the values of *H* for the four barium salts in Tables XVI., XXXII., XXXIII., and XXXIV., we see that of the halides the iodide has the greatest hydrating power, and the chloride the least, while the bromide stands intermediate between the other two. The nitrate has the least hydrating power.

Since the chloride, bromide, and iodide crystallize each with two molecules of water, we should expect the observed molecular lowering to be greater than the calculated. Experimental results confirm this.

Cobalt Chloride.

An approximately two normal solution was first made up. A portion of this was diluted to convenient strength, and the cobalt determined electrolytically.

Cobalt chloride crystallizes with 6 molecules of water, and, like the other chlorides with the same amount of water of crystallization, has a large hydrating power. The results are just what we should expect.

Table XXXV.—Freezing Point Measurements.

m.	Δ.	Δ/*m.*	*i.*	*α.*
0.01	0.06241	6.241	.....	.....
0.025	0.1394	5.5786	2.9992	99.96
0.05	0.2609	5.2186	2.8057	90.28
0.075	0.3356	5.1413	2.7641	88.20
0.10	0.5110	5.1100	2.7473	87.36
0.25	1.3040	5.2160	2.8043	
0.50	2.8371	5.6743	3.0507	
0.75	4.5860	6.1147	3.2874	
1.00	6.7157	6.7157	3.6105	
1.5	12.1308	8.0871	4.3532	
2.0	17.7342	8.8671	4.7672	

Table XXXVI.—Conductivity Measurements.

μ_∞ 0° = 117 (Jones and Bassett)[1].

V.	μ_v.	*α.*
100	113.06	96.63
40	104.86	89.62
20	99.30	84.80
13.34	96.00	82.05
10	92.26	78.85
4	83.79	71.61
2	73.86	63.14
1.334	66.15	56.54
1	59.58	50.92
0.667	48.59	41.53
0.5	38.51	32.91

Table XXXVII.—Specific Gravity Measurements.

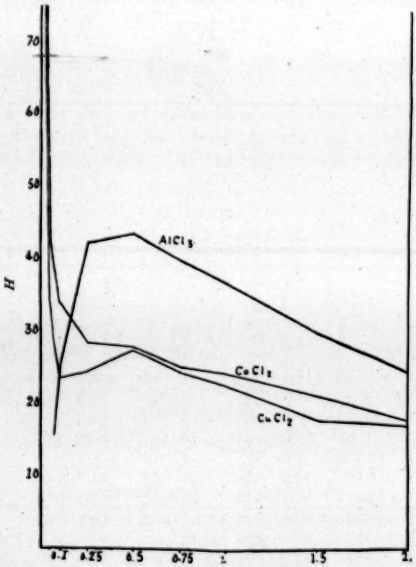
m.	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent of correction.
0.01	1.001159	1001.159	1.299	999.860	0.014
0.025	1.003052	1003.052	3.247	999.805	0.019
0.05	1.006065	1006.065	6.495	999.5703	0.043
0.075	1.009190	1009.190	9.7425	999.447	0.055
0.10	1.012386	1012.386	12.990	999.396	0.060
0.25	1.03049	1030.491	32.475	998.016	0.19
0.50	1.05492	1054.924	64.95	989.974	1.00
0.75	1.09118	1089.180	97.425	991.655	0.83
1.00	1.11847	1118.471	129.90	988.571	1.14
1.5	1.17502	1175.026	194.85	980.176	1.98
2.0	1.23637	1236.376	25.98	976.576	2.34

[1] THIS JOURNAL, **33**, 567 (1905).

Table XXXVIII.—Hydrates.

m.	*a.*	*L.*	$\Delta/m.$	*L′.*	*M.*	*H.*
0.025	89.62	5.1938	5.5786	5.5776	3.822	152.88
0.05	84.87	5.0717	5.2186	5.2164	2.122	42.44
0.075	82.05	4.9122	5.1413	5.1385	2.444	33.68
0.10	78.85	4.7932	5.1100	5.1070	3.413	34.13
0.25	71.61	4.7098	5.2160	5.2057	5.292	28.31
0.50	63.41	4.2088	5.6743	5.6176	13.93	27.86
0.75	56.54	3.9632	6.1417	5.9937	18.22	25.09
1.00	50.92	3.7542	6.7157	6.6394	24.14	24.14
1.5	41.53	3.4049	8.0871	7.9270	31.69	21.1
2.0	32.91	3.0842	8.8671	8.6594	35.76	17.88

It will be noted, first of all, that the freezing point lowerings for all concentrations are greater than for any of the salts



Concentration.

Fig. V.

thus far studied, and hence there is a correspondingly greater difference between the observed and calculated lowerings. The amount of water combined with the salt increases regularly from 0.05 normal to the most concentrated solution, as shown by Fig. VI. The hydration per molecule decreases rapidly in the most dilute solutions, and approaches a constant value at 0.25 normal. For the curve for hydrates, see Fig. V.

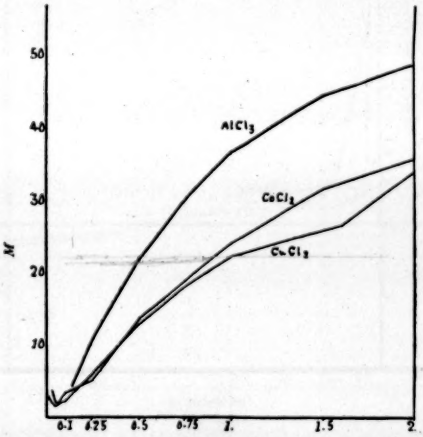


Fig. VI.

Cobalt Nitrate.

Cobalt nitrate, like cobalt chloride, crystallizes with 6 molecules of water, and we should expect it to have hydrating power of the same order of magnitude. The data given in the following tables show that such is the case. What has been said regarding cobalt chloride applies equally well to the nitrate.

The curves for the values of H and M are found in Figs. VII. and VIII., respectively.

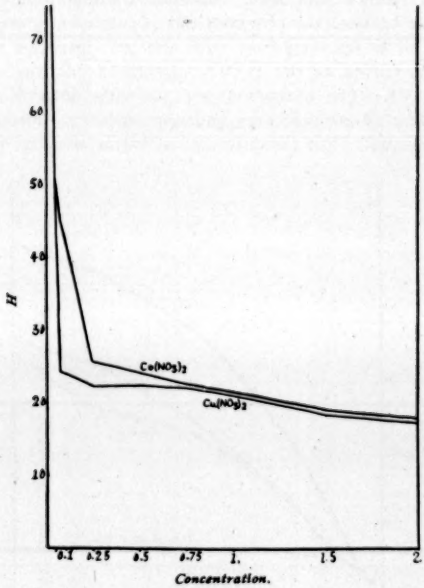


Fig. VII.

Table XXXIX.—Freezing Point Measurements.

m.	Δ.	Δ/*m.*	*i.*	*α.*
0.10	0.0553	5.5300	2.9731	98.65
0.025	0.1341	5.3640	2.8731	93.65
0.05	0.2572	5.1434	2.7652	88.26
0.075	0.3812	5.0826	2.7218	86.09
0.10	0.5005	5.0050	2.7096	85.48
0.25	1.2705	5.0082	2.7323	
0.50	2.708	5.417	2.9125	
0.75	4.338	5.784	3.1099	
1.00	6.220	6.220	3.3441	
1.5	10.888	7.192	3.8668	
2.0	18.863	9.431	5.0701	

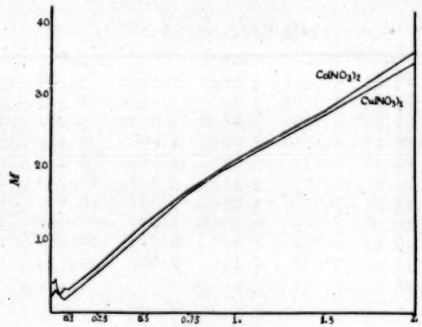


Fig. VIII.

Table XL.—Conductivity.

μ_∞ 0° = 117.6.[1]

V.	μ_v.	α.
100	108.66	92.40
40	100.69	85.62
20	96.12	81.73
13.334	91.67	77.95
10	89.94	76.48
4	81.48	69.28
2	72.94	62.02
1.333	65.32	55.54
1	58.89	50.08
0.668	47.57	40.45
0.5	37.10	31.55

Table XLI.—Specific Gravity Measurements.

m.	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent of correction.
0.01	1.001496	1001.496	1.830	999.652	0.033
0.025	1.003863	1003.863	4.577	999.286	0.071
0.05	1.007579	1007.579	9.154	998.425	0.157
0.075	1.011289	1011.289	13.731	997.558	0.244
0.10	1.015084	1015.084	18.308	996.776	0.322
0.25	1.03737	1037.37	45.77	991.603	0.83
0.5	1.07415	1074.15	91.54	982.61	1.73
0.75	1.11204	1110.04	137.31	972.73	2.72
1.00	1.14612	1146.12	183.08	963.04	3.69
1.5	1.21720	1217.20	274.62	942.58	5.74
2.0	1.28576	1285.76	366.16	919.60	8.04

[1] This Journal, **33**, 569 (1905).

Table XLII.—Hydrates.

m.	*α.*	*L.*	*Δ/m.*	*L′.*	*M.*	*H.*
0.025	85.62	5.0451	5.3640	5.3602	3.266	130.6
0.05	81.73	4.9003	5.1434	5.1354	2.544	50.8
0.075	77.95	4.7597	5.0826	5.0702	3.402	45.3
0.10	76.48	4.7050	5.0050	4.9889	3.161	31.6
0.25	69.28	4.437	5.082	5.0296	6.445	25.8
0.5	62.02	4.167	5.417	5.323	12.070	24.1
0.75	55.54	3.926	5.784	5.627	16.880	22.5
1.00	50.08	3.723	6.220	5.990	21.020	21.0
1.5	40.45	3.364	7.192	6.779	27.980	18.7
2.0	31.55	3.033	9.431	8.607	30.123	18.0

Copper Chloride.

Diluted portions of the mother solution were taken and the copper in them determined electrolytically.

While copper chloride crystallizes with two molecules of water, its power to combine with water is of the same order of magnitude as that of cobalt chloride and cobalt nitrate, as may be seen in the curves, Figs. V. and VII.

The total amount of water combined with the electrolyte passes through a minimum at about 0.05 normal and then increases rapidly with increase in concentration. This is seen in Fig. VI.

Table XLIII.—Freezing Point Measurements.

m.	*Δ.*	*Δ/m.*	*i.*	*α.*
0.01	0.05703	5.7030	.....	.....
0.05	0.24944	4.9888	2.6821	84.10
0.075	0.37075	4.9433	2.6576	80.82
0.100	0.48665	4.8665	2.6164	
0.25	1.2237	4.894	2.6316	
0.50	2.669	5.338	2.8701	
0.75	4.245	5.661	3.0436	
1.00	5.994	5.994	3.2228	
1.50	10.105	6.737	3.6220	
2.0	15.294	7.647	4.1112	

Table XLIV.—Conductivity Measurements.

μ_∞ 0° = 120 (Jones and Bassett).[1]

V.	μ_v.	α.
100	110.55	92.12
20	95.88	79.98
13.34	93.27	77.72
10	90.21	75.17
4	80.20	66.83
2	69.08	57.56
1.334	61.03	50.86
1	54.01	45.00
0.6666	41.81	34.84
0.5	31.56	26.30

Table XLV.—Specific Gravity Measurements.

m.	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent of correction.
0.01	1.001208	1001.208	1.345	999.863	0.013
0.05	1.006370	1006.370	6.725	999.645	0.035
0.075	1.009264	1009.264	10.0875	999.176	0.084
0.10	1.012614	1012.614	13.450	999.164	0.263
0.20	1.030991	1030.991	33.625	997.366	0.263
0.50	1.051479	1061.479	67.25	994.229	0.57
0.75	1.090912	1090.91	100.87	990.037	0.99
1.00	1.120249	1120.24	134.5	985.749	1.42
1.50	1.177618	1177.61	201.75	975.868	2.41
2.0	1.234551	1234.55	269.0	965.55	3.44

Table XLVI.—Hydrates.

m.	α.	*L.*	Δ/m.	*L'.*	*M.*	*H.*
0.05	79.98	4.8352	4.9888	4.9871	1.693	33.85
0.075	77.72	4.7511	4.9433	4.9392	2.116	28.21
0.10	75.17	4.6563	4.8665	4.8695	2.354	23.54
0.20	66.83	4.3460	4.8949	4.8821	6.091	24.36
0.50	57.56	4.0012	5.3384	5.3076	13.67	27.34
0.75	50.86	3.7519	5.6611	5.5748	18.17	24.22
1.00	45.00	3.5340	5.9945	5.9088	22.33	22.33
1.50	34.84	3.1560	6.7370	6.5747	26.66	17.78
2.00	26.30	2.8383	7.6470	7.3836	34.20	17.10

[1] THIS JOURNAL, **33**, 576 (1905).

Copper Nitrate.

The mother solution of the salt was diluted to convenient strength and the copper determined electrolytically.

Copper nitrate crystallizes with 6 molecules of water and, therefore, should give us hydration of the same order of magnitude as that found for the nitrate of cobalt and nickel, which crystallize with the same amount of water. Reference to Table L. will show that this is the fact. The minimum for the total amount of combined water is pronounced and lies between 0.075 and 0.25 normal. The hydration per molecule decreases rapidly with increase in concentration to 0.25 normal, and then becomes approximately constant.

The curves representing the values of H and M are given in Figs. VII. and VIII., respectively.

Table XLVII.—Freezing Point Measurements.

m.	Δ.	Δ/m.	i.	α.
0.01	0.05736	5.7365	3.0841	.....
0.025	0.13852	5.5401	2.9785	98.92
0.05	0.25540	5.1081	2.7463	87.31
0.075	0.36979	4.9306	2.6508	82.54
0.25	1.221	4.885	2.6264	81.32
0.5	2.589	5.178	2.7841	
0.75	4.190	5.587	3.0039	
0.935	5.512	5.895	3.1696	
1.50	10.284	6.856	3.6861	
2.0	16.89	8.44	4.5419	

Table XLVIII.—Conductivity Measurements.

μ_∞ 0° = 118.[1]

V.	μ_v.	α.
100	108.84	92.24
40	101.2	85.76
20	95.7	81.10
13.34	91.86	77.85
4	79.4	57.29
..	69.8	.....
1.334	62.0	52.54
1.0695	56.89	48.21
0.667	44.0	37.29
0.5	33.47	28.36

[1] This Journal, **33**, 578 (1905).

Table XLIX.—Specific Gravity Measurements.

m.	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent. of correction
0.01	1.001504	1001.5049	1.876	999.628	0.037
0.025	1.004076	1004.0764	4.692	999.384	0.061
0.05	1.007859	1007.8599	9.384	998.4759	0.152
0.075	1.011715	1011.7155	14.076	997.6395	0.236
0.25	1.040290	1040.2903	46.920	993.370	0.663
0.50	1.07723	1077.230	93.840	983.390	1.66
0.75	1.11469	1114.699	140.76	973.930	2.607
0.935	1.14262	1142.627	174.48	968.140	3.188
1.5	1.22618	1226.183	281.52	944.660	5.53
2.0	1.29262	1292.623	375.36	917.26	8.27

Table L.—Hydrates.

m.	*a.*	*L.*	$\Delta/m.$	*L'.*	*M.*	*H.*
0.025	75.76	5.0502	5.5401	5.5368	4.882	195.2
0.05	81.10	4.8769	5.1081	5.1005	2.435	48.7
0.075	77.85	4.7560	4.9306	4.9188	1.839	24.5
0.25	67.29	4.363	4.885	4.852	5.607	22.4
0.50	59.15	4.060	5.178	5.092	11.261	22.5
0.75	52.54	3.814	5.587	5.441	16.612	22.15
0.935	48.21	3.653	5.895	5.708	19.953	21.3
1.50	37.29	3.247	6.856	6.447	27.575	18.38
2.0	28.36	2.914	8.44	7.749	34.65	17.32

Nickel Nitrate.

The nickel was determined electrolytically in diluted portions of the mother solution.

The hydrating power of nickel nitrate is of the same order of magnitude as that of cobalt and copper nitrates, which crystallize with the same amounts of water (see Fig. IX.). The total combined water passes through a minimum at 0.05 normal and then increases rapidly with increasing concentration (see Fig. X.).

Table LI.—Freezing Point Measurements.

m.	Δ.	Δ/*m.*	*i.*	*a.*
0.01	0.0550	5.5070	2.9607	98.03
0.025	0.1299	5.1960	2.7950	89.75
0.05	0.2487	4.9745	2.6744	83.72
0.075	0.3664	4.8854	2.6265	81.32
0.10	0.4960	4.9602	2.6667	
0.25	1.251	5.003	2.6901	
0.5	2.652	5.305	2.8524	
0.75	4.213	5.618	3.0205	
1.00	6.101	6.101	3.2801	
1.5	10.576	7.051	3.7910	
2.0	17.050	8.523	4.5334	

Table LII.—Conductivity Measurements.

μ_∞ 0° = 117.2.[1]

V.	μ_v.	*a.*
100	106.77	91.10
40	100.31	85.58
20	93.57	79.83
13.34	89.74	76.77
10	87.84	74.94
4	80.07	68.31
2	71.44	60.95
1.334	64.06	54.65
1.0	57.38	48.95
0.667	45.79	39.06
0.5	35.61	30.38

Table LIII.—Specific Gravity Measurements.

m.	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent of correction.
0.01	1.001521	1001.521	1.8278	999.693	0.030
0.025	1.003882	1003.882	4.5695	999.312	0.068
0.05	1.007792	1007.792	9.139	998.653	0.134
0.075	1.011541	1011.541	13.7085	997.029	0.216
0.10	1.015307	1015.377	18.278	997.029	0.291
0.25	1.03837	1038.37	45.695	992.68	0.732
0.5	1.07611	1076.11	91.390	984.72	1.527
0.75	1.11310	1113.10	137.08	976.01	2.39
1.0	1.14562	1145.62	182.78	962.88	3.71
1.5	1.22134	1221.34	274.17	947.17	5.28
2.0	1.29459	1294.59	365.56	929.03	7.09

[1] THIS JOURNAL, **33**, 574 (1905).

Table LIV.—Hydrates.

m.	*a.*	*L.*	$\Delta/m.$	*L'.*	*M.*	*H.*
0.05	79.83	4.8296	4.9745	4.9679	1.545	30.9
0.075	76.0	4.7084	4.8854	4.8749	1.797	25.3
0.075	76.57	4.7084	4.8854	4.8749	1.897	25.3
0.10	74.94	4.6477	4.9675	4.8721	2.560	25.6
0.25	68.31	4.401	5.0036	4.9670	6.329	25.3
0.50	60.95	4.127	5.305	5.225	11.672	23.3
0.75	54.65	3.894	5.618	5.484	16.102	21.4
1.00	48.95	3.700	6.102	5.875	20.561	20.5
1.5	39.06	3.313	7.051	6.679	27.998	18.6
2.0	30.38	2.990	8.525	7.921	34.58	17.3

Before going farther, it will be interesting to note the great similarity between the salts of cobalt, copper, and nickel which we have just studied. Solutions of the same concentrations were used in all five salts.

Reference to Figs. VI., VIII., and X. will show at a glance the close relation between the amounts of water held in combination by these salts, whether they are chlorides or nitrates. We are not surprised at this, since, with the exception of copper chloride, all crystallize with 6 molecules of water. In fact, we found it impossible to put more than two curves on one sheet, so closely did the values agree. From the minimum in the most concentrated solutions studied, the magnitude of the hydrating power is a linear function of the concentration. In other words, each hydrate has its own definite composition, which varies with every concentration.

The curves representing the hydration per molecule (Figs. V., VII., and IX.) show the same striking similarity. They are almost asymptotic with the two coördinates. The hydration per molecule decreases very rapidly, for the very dilute solutions, to approximately the same concentration, when they become nearly constant for further increase in concentration.

Two conclusions are to be drawn from these relations. It will be noted that the molecular hydration and the total amount of water held in combination are the same for any two salts containing a common cation. It seems most probable that if the two anions, $\overline{Cl}$ and $\overline{NO_3}$, possessed very different hydra-

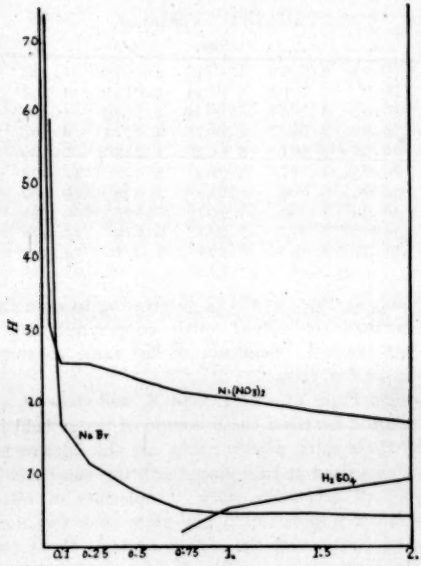


Fig. IX.

ting power, this influence would manifest itself. It is a well-known fact that organic acids possess little or no hydrating power, and in the work which we have done upon the strong acids—hydrochloric, nitric, and sulphuric—this has been found to hold in the dilute solutions, where the dissociation is practically complete.

This would lead us to conclude that *the hydrating power of any salt is primarily a function of the cation.*

In the discussion of the nitrates and chlorides of the alkaline earth group, attention was called to the fact that the hydrating power of those salts is an inverse function of the atomic volumes.

In the case of the salts of cobalt, copper, and nickel which we have studied, we have to do with cations which have approximately the same atomic volumes.

As stated by Ostwald,[1] the migration velocity of an organic acid decreases with increase in the mass of the anion, as well as with increase in the mass of the cation in case of the organic bases. We should expect, then, to obtain larger values for conductivity than those given by the alkaline earth metals. Experiment shows the opposite to be the fact. We are, therefore, forced to believe that the effect of the atomic volume of the ions upon the conductivity is more than compensated for by the relatively large volume of the ionic complex.

Bredig[2] pointed out the fact that the migration velocities of elementary cations are a periodic function of the atomic weights. When plotted in a curve, where the ordinates represent velocities and the abscissas the atomic weights, it will be seen that the alkali metals lie very near the maxima of the curve, along with the halogens. At the extreme minima we find aluminium and chromium. Slightly above these lie the metals of the copper group, zinc, and cadmium; while still higher are to be found the metals of the alkaline earths.

The significance of this periodic relation between the migration velocities of the cations and the atomic weights has never been satisfactorily explained.

We believe that we have found the cause of this phenomenon. Of two ions or ionic complexes of different volumes, that one will meet with less friction on moving through the solution which has the smaller volume. Consequently, it will have the greater velocity. On the other hand, the greater the volume, the greater will be the friction to be overcome by the ion, and, hence, the smaller the velocity. Therefore, we should expect to find that those salts which crystallize with little or no water of crystallization give greater values for conductivity than those crystallizing with a greater amount.

It is a well-known law that the conductivity of an electrolyte depends upon the velocities of the ions. These velocities, in turn, depend upon the fluidity and the volume of the

[1] Lehrbuch, **2**, 679.
[2] Z. physik. Chem., **13**, 242 (1894).

ion. The greater the volume, the greater will be the resistance offered to the movement of the ions.

If we consider the alkalis we find that potassium, rubidium, and caesium, which have the largest atomic volumes and whose salts generally crystallize without water, have the greatest migration velocities, while lithium and sodium, which have smaller atomic volumes and whose salts crystallize with two or three molecules of water, have very much smaller migration velocities.

Comparing the members of the calcium group, we find that the atomic volumes increase with increasing atomic weight. The migration velocities of the cations calcium and strontium, whose salts usually crystallize with 6 molecules of water, are approximately equal to that of the barium cation, whose salts crystallize either with two molecules of water, or water-free. On the other hand, the magnesium cation, of smaller atomic volume, has a slightly smaller migration velocity, due to the more complex composition of its hydrates.

The cations of cobalt, copper, and nickel have approximately the same atomic weights, the same atomic volume, and the same hydrating power. Since these cations have the greatest hydrating power of any which we have studied, we should expect them to have the smallest migration velocities, and such is the case.

Aluminium Chloride.

Special interest is attached to the study of aluminium chloride, owing to the fact that it is a quaternary electrolyte and crystallizes with six molecules of water.

The hydrolytic effect of water upon this salt, in dilute solutions, can be noted in the first two concentrations. The hydrochloric acid liberated is almost completely dissociated at the dilutions in question, thus giving values for L which are considerably higher than would be obtained if the salt were not hydrolyzed. This may be attributed to one of two causes: the very high migration velocity of the hydrogen ion; its inability to form hydrates; or both. It is at about 0.075 normal that the influence due to the hydration of the aluminium cation begins to predominate. Just as we should ex-

pect, the number of molecules of water held in combination by one molecule of the electrolyte is large and increases very rapidly with increase in concentration (see Fig. VI.). In the curve representing the hydration per molecule (Fig. V.), that part representing concentrations between 0.075 and 0.5 normal represents the abnormality in the hydration due to hydrolysis.

A glance at column α (Table LVIII.) shows us that, in spite of the tendency of this salt to hydrolyze, the dissociation decreases very rapidly with increase in concentration. This is just what might be predicted. Its atomic volume is very small and the hydrating power of its cation very large. Therefore, it should have a very small migration velocity.

Table LV.—Freezing Point Measurements.

m.	Δ.	Δ/m.	i.	α.
0.01	0.712	7.1200	3.8279	94.26
0.025	0.1623	6.4940	3.4193	80.64
0.05	0.3053	6.1060	3.2827	76.09
0.075	0.4511	6.0153	3.2340	74.46
0.10	0.4511	6.0850	3.2704	
0.25	1.6604	6.641	3.5708	
0.50	3.9446	7.889	4.2415	
0.75	7.1339	9.511	5.1137	
1.00	11.795	11.795	6.341	
1.5	25.5[1]	17.000	9.1398	
2.0	48.5[1]	24.25	13.037	

Table LVI.—Conductivity Measurements.

μ_∞ 0° = 170.[2]

V.	μ_v.	α.
100	156.48	92.04
40	141.24	83.08
20	130.44	76.72
13.334	126.66	74.50
10	122.07	71.80
4	106.90	62.88
2	88.60	52.11
1.333	75.02	44.12
1	61.93	36.42
1.6667	41.62	24.48
0.5	25.47	14.98

[1] These freezing points were determined by means of an alcohol thermometer, and freezing mixtures of solid carbon dioxide and ether.

[2] This Journal, **31**, 333 (1904).

Table LVII.—Specific Gravity Measurements.

m.	Sp. gr.	$W_{sol.}$	$W_{salt.}$	W_{H_2O}.	Per cent of correction.
0.01	1.00104	1001.04	1.3345	999.71	0.029
0.025	1.00282	1002.82	3.3625	999.49	0.051
0.05	1.00588	1005.88	6.6725	999.21	0.079
0.075	1.00870	1008.70	10.0087	998.70	0.130
0.1	1.01158	1011.58	13.345	998.24	0.176
0.25	1.02911	1029.11	33.36	995.75	0.425
0.55	1.05706	1057.06	66.725	990.33	0.966
....	1.08431	1084.31	100.087	988.22	1.57
1.00	1.11054	1110.54	133.45	977.09	2.29
1.5	1.16308	1163.08	200.175	962.905	3.70
2.00	1.21378	1213.78	266.90	946.88	5.31

Table LVIII.—Hydrates.

m.	*α.*	*L.*	*Δm.*	*L′.*	*M.*	*H.*
0.01	92.04	6.9958	7.1200	7.1180	.....	....
0.025	83.08	6.4958	6.4940	6.4907	.....	....
0.05	76.72	6.1409	6.1060	6.1012	.....	....
0.075	74.50	6.0111	6.1526	6.1447	.....	....
0.10	71.80	5.8664	6.1560	6.1452	2.52	25.2
0.25	62.88	5.368	6.641	6.613	10.54	42.16
0.5	44.12	4.321	9.511	9.362	9.91	39.88
1.00	36.42	3.892	11.795	11.523	36.78	36.78
1.5	24.48	3.225	17.000	16.369	44.60	29.33
2.0	14.98	2.695	24.25	22.963	49.03	24.51

Sodium Bromide.

Dilute portions of the mother solution were standardized volumetrically by Volhard's method. This salt differs from those preceding in that it is a binary electrolyte and crystallizes with two molecules of water. A study of Table LXII. brings out the same general results. The observed molecular lowering passes through a minimum between 0.5 and 0.75 normal. The minimum in the total amount of combined water occurs at 0.10 normal. From the amounts of water which combine with one gram molecule of the salt, it will be seen that the sodium cation has nearly the same hydrating power in dilute solutions as do the cations of the calcium and copper groups.

The atomic volume of sodium is slightly more than half

that of potassium. Its hydrating power, however, for the more dilute solutions is much greater. If, then, the amount of hydration of the sodium ion is more than sufficient to compensate for the inverse volume relations, we should expect the migration velocity of sodium to be less than that of potassium. This has been found to be the case.[1]

The atomic volume of sodium is also slightly less than that of calcium, and considerably less than those of strontium and barium; yet, owing to the greater hydration of the cations of the calcium group, its migration velocity is greater.

For the curves representing the values of H and M, see Figs. IX. and X.

Table LIX.—Freezing Point Measurements.

m.	Δ.	Δ/m.	i.	α.
0.01	0.03936	3.9360	.....	.....
0.025	0.0952	3.8090	2.0478	104.78
0.05	0.1863	3.7260	2.0032	100.32
0.075	0.2727	3.636	1.9548	95.48
0.10	0.3572	3.572	1.9204	92.04
0.25	0.885	3.543	1.9049	90.49
0.50	1.787	3.574	1.9215	
0.75	2.696	3.595	1.9327	
1.00	3.633	3.633	1.9481	
1.5	5.654	3.769	2.0263	
2.00	7.746	3.873	2.0822	

Table LX.—Conductivity Measurements.

μ_∞ 0° = 64.48.[2]

V.	μ_v.	α.
100	61.12	94.78
40	59.02	91.53
20	57.67	89.44
13.334	56.33	87.36
10	55.28	85.73
4	51.08	79.21
2	49.51	76.78
1.333	49.06	76.08
1	47.61	73.83
0.6667	45.50	70.56
0.5	42.70	66.22

[1] Bredig: Z. physik. Chem., **13**, 242 (1894).
[2] This Journal, **34**, 375 (1905).

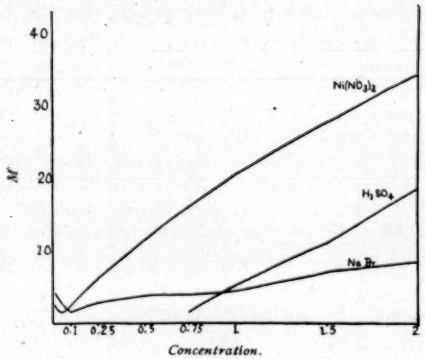


Fig. X.

Table LXI.—Specific Gravity Measurements.

m.	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent of correction.
0.01	1.000732	1000.732	1.030	999.70	0.030
0.025	1.002177	1002.177	2.575	999.602	0.040
0.05	1.004074	1004.074	5.150	998.924	0.107
0.075	1.005972	1005.972	7.725	998.247	0.175
0.10	1.00788	1007.88	10.30	997.58	0.24
0.25	1.01964	1019.64	25.75	993.89	0.61
0.50	1.03908	1039.08	51.50	987.58	1.24
0.75	1.05811	1058.11	77.25	980.86	1.91
1.00	1.07632	1076.32	103.01	973.31	2.66
1.5	1.11963	1119.63	154.51	965.12	3.48
2.00	1.15240	1152.40	206.02	946.38	5.36

Table LXII.—Hydrates.

m.	*a.*	*L.*	$\Delta/m.$	*L'.*	*M.*	*H.*
0.025	91.53	3.5624	3.805	3.8075	3.575	143.0
0.05	89.44	3.5235	3.7260	3.7221	2.963	59.2
0.075	87.36	3.4848	3.636	3.6297	2.217	24.29
0.10	85.73	3.4545	3.572	3.5635	1.700	17.00
0.25	79.21	3.333	3.543	3.521	2.974	11.89
0.50	76.78	3.288	3.574	3.529	3.803	7.60
0.75	76.08	3.275	3.595	3.526	3.961	5.28
1.00	72.83	3.233	3.633	3.536	4.763	4.76
1.5	70.56	3.172	3.769	3.637	7.103	4.73
2.00	66.22	3.101	3.873	3.665	8.547	4.27

Hydrochloric Acid.

Having investigated fifteen salts, we next turned our attention to the study of some of the more common acids.

An approximately three normal solution of hydrochloric acid was prepared. Dilute portions of the mother solution were then titrated against a standard solution of potassium hydroxide free from carbonate. This, in turn, had been standardized by means of a tenth normal solution of freshly prepared oxalic acid. The results are given in Tables LXIII. to LXVI.

A glance at Table LXVI. shows that, for the more dilute solutions, the corrected observed freezing point lowering (L') is less than that calculated from the dissociation. This is due to one of two causes: the very high migration velocity of the hydrogen ion, or its inability to form hydrates.

The minimum in the freezing point lowering occurs at about 0.25 normal. For dilutions greater than 0.5 normal, there is no evidence of hydration. At 0.5 normal, however, the hygroscopic property of the molecular hydrochloric acid begins to predominate over the effect of decrease in dissociation. From this point the amount of combined water increases with increase in concentration. The corresponding values of H differ from those of the other electrolytes thus far studied in that they, also, increase as the concentration increases.

The values of H and M, for hydrochloric acid, are plotted in Figs. I. and II.

Table LXIII.—Freezing Point Measurements.

m.	Δ.	Δ/m.	i.	α.
0.025	0.0902	3.6080	1.9377	93.97
0.05	0.1799	3.5980	1.9344	93.44
0.075	0.2681	3.5752	1.9221	92.21
0.10	0.3567	3.5670	1.9177	91.77
0.25	0.8862	3.5450	1.9059	90.59
0.50	1.841	3.682	1.9794	
0.75	2.852	3.804	2.0450	
1.00	3.975	3.975	2.1372	
1.50	6.452	4.301	2.3123	
2.00	9.367	4.683	2.5177	

Table LXIV.—Conductivity Measurements.

μ_∞ 0° = 236.92.

V.	μ_v.	*α.*
40	233.95	98.75
20	232.60	98.18
13.33	231.87	97.87
10	228.61	96.49
4	222.17	93.77
2	211.79	89.39
1.333	203.28	85.80
1	199.85	84.35
0.667	181.79	76.73
0.5	168.04	70.93

Table LXV.—Specific Gravity Measurements.

m.	Sp. gr.	$W_{sol.}$	$W_{salt.}$	W_{H_2O}.	Per cent of correction.
0.025	1.00034	1000.34	0.911	999.429	0.057
0.05	1.00101	1001.01	1.822	999.188	0.081
0.075	1.00135	1001.35	2.734	998.616	0.138
0.10	1.00180	1001.80	3.645	998.155	0.184
0.25	1.00425	1004.25	9.114	999.136	0.486
0.50	1.00849	1008.49	18.229	990.261	0.973
0.75	1.01264	1012.64	27.343	985.297	1.47
1.00	1.01749	1017.49	36.458	981.032	1.896
1.5	1.02542	1025.42	54.687	970.733	2.92
2.0	1.03414	1034.14	72.916	961.224	3.87

Table LXVI.—Hydrates.

m.	*α.*	*L.*	Δ/*m.*	*L′.*	*M.*	*H.*
0.025	98.75	3.6967	3.6080	3.6060	.....	....
0.05	98.18	3.6861	3.5980	3.5960	.....	....
0.075	97.87	3.6803	3.5752	3.5702	.....	....
0.10	96.40	3.6547	3.5670	3.5610	.....	....
0.25	93.77	3.6041	3.5450	3.5280	.....	....
0.20	.....	3.5021	3.5310	3.6260	1.580	3.16
0.75	85.80	3.455	3.803	3.747	3.33	5.77
1.00	84.35	3.428	3.975	3.899	6.707	6.70
1.5	76.73	3.287	4.301	4.176	11.820	7.88
2.0	70.93	3.179	4.683	4.502	16.32	8.16

Nitric Acid.

A moderately concentrated solution was first made up, care having been taken that the acid used contained none of the oxides of nitrogen in solution.

Dilute portions of this were standardized volumetrically against a solution of potassium hydroxide.

Like hydrochloric acid, dilute solutions of nitric acid exhibit no tendency to form hydrates. No appreciable power to combine with water is manifested until the concentration 0.75 normal is reached. The amount of total combined water, then, increases with increase in concentration. The same results are obtained for the values of H. For curves representing the values of H and M see Figs. III. and IV.

Table LXVII.—Freezing Point Measurements.

m.	Δ.	Δ/m.	i.	α.
0.025	0.09035	3.6140	1.9430	94.30
0.05	0.1791	3.5830	1.9263	92.63
0.075	0.2678	3.5713	1.9200	92.00
0.10	0.3547	3.5470	1.9069	90.69
0.25	0.8869	3.4576	1.9073	90.73
0.50	1.798	3.597	1.9341	
0.75	2.766	3.681	1.9736	
1.00	3.749	3.749	2.0156	
1.5	5.955	3.970	2.1344	
2.0	8.383	4.191	2.2532	

Table LXVIII.—Conductivity Measurements.

μ_∞ 0° = 237.07.

V.	μ_v.	α.
40	234.89	99.08
20	233.88	98.65
13.33	229.66	96.87
10	226.24	95.43
4	222.82	93.99
2	216.63	91.38
1.334	211.43	89.17
1.0	203.72	85.93
0.5	177.15	74.71

Table LXIX.—Specific Gravity Measurements.

m.	Sp. gr.	$W_{sol.}$	$W_{salt.}$	W_{H_2O}.	Per cent of correction.
0.025	1.000926	1000.926	1.576	999.35	0.065
0.05	1.001798	1001.798	3.152	998.64	0.134
0.075	1.002653	1002.653	4.728	997.92	0.207
0.10	1.003496	1003.496	6.304	997.19	0.281
0.25	1.008481	1008.48	15.762	992.71	0.728
0.5	1.01686	1016.86	31.524	985.34	1.465
0.75	1.02503	1025.03	48.280	976.75	2.325
1.00	1.03360	1033.60	63.050	970.55	2.945
2.00	1.06700	1067.00	126.090	940.91	5.909

Table LXX.—Hydrates.

m.	*a.*	*L.*	$\Delta/m.$	*L'.*	*M.*	*H.*
0.025	99.08	3.7028	3.6140	3.6124	.....	....
0.05	98.65	3.6948	3.5830	3.5790	.....	....
0.075	96.87	3.6617	3.5713	3.5640	.....	....
0.10	95.43	3.6348	3.5470	3.5370	.....	....
0.25	93.99	3.6062	3.5476	3.5210	.....	....
0.5	91.38	3.559	3.597	3.544	.....	....
0.75	89.17	3.518	3.680	3.595	1.180	1.57
1.00	85.93	3.450	3.749	3.639	2.880	2.88
2.00	74.71	3.249	4.191	3.944	9.78	4.89

Sulphuric Acid, 98.07.

Dilute portions of the mother solution were titrated against the standard potassium hydroxide used for the previous acids.

The results are given in Tables LXXI. to LXXIV.; the curves in Figs. IX. and X.

In dilute solutions no water is held in combination. The total amount of water held in combination by the acid, and the hydration per molecule, increases with concentration from 0.75 to 2 normal.

Table LXXI.—Freezing Point Measurements.

m.	$\Delta.$	$\Delta/m.$	*i.*	*α.*
0.01	0.04872	4.8720	2.6193	80.96
0.025	0.1179	4.7184	2.5367	76.84
0.050	0.2182	4.3640	2.3462	67.31
0.075	0.3157	4.2099	2.2634	63.17
0.10	0.4043	4.0434	2.1738	58.69
0.25	0.9865	3.9460	2.1215	56.07
0.50	2.0033	4.0066	2.1541	
0.75	3.1174	4.156	2.2346	
1.00	4.379	4.379	2.3544	
1.50	7.265	4.843	2.6042	
2.0	11.296	5.648	3.0365	

Table LXXII.—Conductivity Measurements.

μ_∞ 0° = 485.42.

V.	μ_v.	α.
100	398.34	82.06
40	353.41	72.80
20	335.56	69.13
13.34	323.43	66.63
10	314.42	64.78
4	296.30	61.04
2	281.52	57.99
1.334	271.25	55.88
1.00	259.05	53.37
0.6667	234.38	48.28
0.5	209.28	43.11

Table LXXIII.—Specific Gravity Measurements.

m.	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent of correction.
0.01	1.000719	1000.719	0.980	999.74	0.026
0.025	1.001907	1001.91	2.451	999.45	0.054
0.05	1.003551	1003.55	4.902	998.65	0.135
0.075	1.005152	1005.15	7.353	997.79	0.220
0.1	1.00677	1006.77	9.807	996.97	0.303
0.25	1.01618	1016.18	24.51	991.67	0.832
0.5	1.03218	1032.18	49.03	983.14	1.68
0.75	1.04760	1047.60	73.53	974.07	2.59
1.00	1.06307	1063.07	98.07	964.99	3.50
1.5	1.09345	1093.45	147.11	946.34	5.36
2.0	1.12316	1123.51	196.15	926.99	7.30

Table LXXIV.—Hydrates.

m.	α.	*L.*	Δ/m.	*L.'*	*M.*	*H.*
0.01	82.06	4.9126	4.8720	4.8708	.....	....
0.025	72.80	4.5681	4.7184	4.7159	.....	....
0.05	69.13	4.4316	4.3640	4.3582	.....	....
0.075	66.63	4.3386	4.2099	4.2007	.....	....
0.10	64.78	4.2698	4.0434	4.0312	.....	....
0.25	61.04	4.1306	3.9460	3.9132	.....	....
0.5	57.99	4.017	4.266	3.939	.....	....
0.75	55.88	3.938	4.156	4.048	1.512	2.00
1.0	53.37	3.845	4.379	4.226	5.004	5.00
1.5	48.28	3.656	4.844	4.585	11.257	7.50
2.0	43.11	3.464	5.648[1]	5.236	18.801	9.40

[1] Jones and Getman: Z. physik. Chem., **46**, 272 (1903).

A comparison of Figs. I., III., and IX. shows that the hydrating powers of hydrochloric and sulphuric acids are of approximately the same order of magnitude, while that of nitric acid is slightly less.

Figs. II., IV., and X., representing the total amounts of combined water for the three acids, show that the same relation holds here as for the hydrates.

Discussion.

Fifteen salts and three strong acids have been studied in this investigation. We have worked with solutions covering a range of concentration from 0.01 to 2.0 normal; at one extremity are found to predominate, in a very pronounced manner, those influences due to the ions; at the other, those due to the molecules also manifest themselves. In this way we have attempted to compare the relative effects of the ions and the molecules upon the molecular lowering of the freezing point and the dissociation.

Comparing, first of all, the freezing point lowerings for any given solution, it is found that, without exception, the molecular lowering calculated from the dissociation decreases regularly with increasing concentration. Naturally, this follows from the fact that the decrease in dissociation is regular throughout. On the other hand, the corrected observed freezing point lowering decreases very rapidly in the dilute solutions, passes through a very pronounced minimum, and then increases as the concentration increases. A glance at the tables of the hydrates shows that in every case the observed molecular lowering produced by any salt is greater than the calculated lowering based on conductivity measurements.

If there were no hydration, we should expect the observed and the calculated molecular lowerings to be equal, except for the difference due to the influence of the friction between the ion and the solvent. The nearest approach to this condition which we have met is found in the most concentrated solutions of barium nitrate. Here the observed molecular lowering is about one per cent greater than the calculated value.

An equally satisfactory agreement was found by Jones and Stine for solutions of potassium chloride, which, likewise, crystallizes without water.

The values of M and H also show that the abnormality of the freezing point lowering in the dilute solutions is greatly augmented by the relatively great hydrating power of the ions.

Since, then, the hydration of the ion increases with increase in dilution, the volume and mass of the ionic complex is greater, the more dilute the solution; and, therefore, the greater will be the resistance to be overcome by the ion as it moves through the solvent. This being the case, the dissociation as measured by the conductivity method will be *less* than the true dissociation, and the abnormality in the dissociation measured will increase with increasing dilution.

The effect produced by adding more of the given electrolyte will be to break down these larger hydrates into simpler ones with smaller volume, thus decreasing the resistance to the motion of the hydrated ion.

This agrees well with the results of Jones and Uhler.[1] They found that the number of ether waves of different wave length with which a given particle will vibrate in resonance decreases with increasing dilution, thereby producing a narrowing of the absorption bands. On the other hand, the addition of more of the same electrolyte, or a strong dehydrating agent, decreases the complexity of the hydrate, thereby decreasing its period. As a result, the particles are free to vibrate in resonance with a greater number of wave lengths, and the absorption bands widen.

It will be seen that, with the exception of magnesium chloride, the value of M, the total amount of water held in combination by one molecule of the electrolyte, decreases rapidly in the dilute solutions, passes through a minimum, and then becomes a linear function of the concentration.

The hydration per molecule decreases rapidly, to approximately the same concentration which corresponds to a minimum in the freezing point lowering, and then remains practically constant as the concentration increases.

[1] THIS JOURNAL, **37**, 126 (1907); Carnegie Inst. (Washington), Memoir No. 60.

Eliminating the hydration due to the ions, the hydration per molecule in solution over a given range of temperature is constant, just as the amount of water with which that same salt will crystallize from solution is constant for a given range of temperature. This relation is best illustrated by the curves representing the values of *H*. They are almost asymptotic to the coördinates.

Having found that the ions of a salt are hydrated, the next question which arises is this: Is it the cation or the anion which has the greater hydrating power?

Nernst, Garrard, and Oppermann,[1] in a study of the concentration changes which take place in an indifferent substance during electrolysis, have calculated that the ions $\overline{SO}_4$, $\overline{Cl}$, $\overline{Br}$, and $\overline{NO}_3$ drag with them 9, 5, 4, and 2.5 molecules of water, respectively.

It is seen from a study of the chlorides and nitrates of the copper group, each of which crystallizes with 6 molecules of water (copper chloride alone separating with two molecules), that the hydration per molecule is approximately the same for all of these salts. If, as Nernst and his coworkers have found, the hydrating power of the $\overline{NO}_3$ ion is only one-half that of the $\overline{Cl}$ ion, then we should expect the influence of the hydrating power of these two anions to manifest itself in the hydrating power of the salts in question, and especially so since the three cations are so nearly alike chemically. On the basis of this reasoning we are forced to conclude that the *hydrating power of any salt is primarily a function of the cation.*

We do not deny that the anions are capable of forming hydrates; but, if they do, experiments lead us to believe that they have this power only to a relatively slight degree.

We have noted also this striking relation. It is well known that if the atomic volumes of the elements are plotted as ordinates against the atomic weights as abscissas, there exists between them a periodic relation. At the maxima of the curve are the alkali metals. The three elements having the largest

[1] Göttingen Nachr., 1900, p. 86.

atomic volumes are potassium, rubidium, and caesium. Salts of these metals usually crystallize from aqueous solution in the anhydrous form, and as experiments have shown, they have very slight hydrating power in solution. Lithium and sodium, some of whose salts crystallize with two and three molecules of water, have much smaller atomic volumes.

At the minimum of the third section of the atomic weight curve we find the elements strontium, iron, cobalt, copper, and nickel. The salts of these metals crystallize with large amounts of water and show great hydrating power in solution. Aluminium, which has less than half the atomic weight of iron, but slightly greater atomic volume, lies at the second minimum. Its salts crystallize with 8 and 9 molecules of water and show great hydrating power in solution.

Comparing the metals of the alkaline earth group we find that barium, whose salts crystallize with two molecules of water or water-free, has the largest atomic volume. The other members of this group form salts which crystallize with 6 molecules, calcium nitrate excepted. The magnesium cation, which has the smallest atomic volume, has the greatest hydrating power in solution; the strontium cation, which has the largest atomic volume, has a smaller hydrating power than does the calcium cation, whose atomic volume is slightly less.

This is conclusive evidence that the *hydrating power of the cation is an inverse function of its atomic volume.*

That the velocities of the ions are an inverse function of their mass (and perhaps of their volumes) is an established fact. Experimental evidence, however, seems at variance with this statement. We should expect those ions which have the smallest atomic volumes to have the greatest migration velocities. On the contrary, we find that potassium, rubidium, and caesium have the greatest migration velocities ($\overset{+}{H}$ and $\overset{-}{OH}$ excepted), while the ions of the iron and copper groups, with very small atomic volumes, have the smallest migration velocities.

A glance at the two curves representing the relation between atomic volume and atomic weights, and between migra-

tion velocities and atomic weights, shows at once the cause of this apparent anomaly. It has been shown that those elements which have the smallest atomic volumes have the greatest hydrating power, and *vice versa*. We see, then, that *those ions which have the smallest migration velocities have also the greatest hydrating power.*

A somewhat detailed comparison of the members of the different groups will bring out this idea more clearly.

The atomic volumes of potassium, rubidium, and caesium increase rapidly with increasing atomic weights, and, as a rule, their salts crystallize without water. We should expect, then, the potassium ion to have the greatest migration velocity, and the caesium ion to have the smallest. Experiments show that they have approximately the same migration velocities. Sodium and lithium, whose atomic volumes are less than half that of potassium, have migration velocities which are only about two-thirds that of potassium. It will be remembered that sodium and lithium form salts which may crystallize with 2 and 3 molecules of water, respectively. Hence we may assume that the increase in volume of the sodium and lithium ions, due to the formation of a relatively large hydrate, decreases the velocity of those ions to a far greater extent than the slight hydration of the large potassium ion decreases the velocity of that ion.

The atomic volume of lithium is about one-half that of sodium, and the maximum amount of water with which lithium salts crystallize from solution is 3 molecules, whereas the maximum for sodium salts is 2 molecules. Since the ratio of 2:3 represents approximately the ratio of the hydrating power of the two ions in solution, we should expect the effect, upon the velocity, of the greater increase in the volume of the small lithium ion, due to its hydration, to compensate somewhat for the smaller increase in the volume of the larger sodium ion. Experiment shows that the migration velocities are nearly equal.

The same relation holds for the metals of the alkaline earth group. The atomic volumes increase with increasing atomic weight. The migration velocities of the cations cal-

cium and strontium, whose salts crystallize with 6 molecules of water, are approximately equal to that of the barium cation, whose salts crystallize either with 2 molecules of water, or water-free. On the other hand, the magnesium cation, which has one-half the atomic volume of the calcium ion, has nearly the same migration velocity, due to compensation between the atomic volumes and the hydration of the ions.

The calcium ion has a slightly greater atomic volume than sodium, yet, owing to its much greater hydrating power, its migration velocity is considerably less.

The cations of copper, cobalt, and nickel have nearly the same atomic volumes and the same hydrating power. We should expect them to have the same migration velocity, and such is the case.

The atomic volumes of the halogens, chlorine, bromine, and iodine, are approximately the same. If their ions are hydrated we should expect them to combine with the same amount of water, and, therefore, they should give migration velocities of the same order of magnitude. This has been found to be the case. The atomic volume of fluorine has not been determined, but from its position on the migration velocity curve we should infer that its atomic volume is smaller than that of the halogens, and that its ion possesses a considerable degree of hydrating power.

Further, it will be noted that the migration velocities of the halogens are almost identical with those of the alkalis standing next above them in order of atomic weights, whereas their atomic volumes are very much smaller. This leads us to believe that the compensation, which brings about an equalization of the migration velocities of the two groups, is due to the increase in volume of the alkali ions by hydration.

The silver ion alone of all the metallic elements for which satisfactory data can be found presents an exception. It has a small atomic volume, and its salts crystallize from solution without water. We should expect it to have but slight hydrating power in solution and it should, therefore, have a high migration velocity, but this has been found to be slightly less than that of the halogens.

According to the law of Raoult, the lowering of the freezing point of a given weight of solvent by a dissolved substance is directly proportional to the amount of the substance dissolved, providing that substance is a non electrolyte. In the case of electrolytes the lowering produced by gram molecular weights of the dissolved substances are greater than those produced by gram molecular weights of non electrolytes. This abnormality in the case of electrolytes is explained by the fact that an ion and a molecule lower the freezing point to the same extent.

The fact is that the freezing point method gives us a relation between the amount of solvent acting as such and the number of dissolved particles, whether they are molecules or ions.

Having determined the freezing point lowering for any concentration of a given electrolyte, it is an easy matter to calculate the amount of dissociation. For binary electrolytes α is obtained from the expression $\alpha = i - 1$; where i is the van't Hoff i. For ternary electrolytes, $\alpha = \frac{i-1}{2}$, and for quaternary electrolytes $\alpha = \frac{i-1}{3}$.

We have calculated the values of α from the molecular lowerings of all the solutions studied, for the dilute solutions up to the concentration at which the molecular lowering passes through a minimum. Beyond this concentration the molecular lowering of the freezing point increases, due to hydration, and, consequently, the calculated dissociation would increase. For that reason the values of α have not been calculated.

In the case of every salt studied, without exception, *the dissociation as calculated from the freezing point lowering is higher than the dissociation as calculated from the conductivity measurements.*

This will be seen by comparing the values obtained for α in the tables representing the freezing point and conductivity measurements for each salt.

If there were no hydration, these values should be equal. Since the freezing point measurements give us the most ac-

curate relation between the amount of the actual solvent and the number of dissolved particles, it, therefore, must give us the most accurate measure of the dissociation, when hydration is taken into account.

The conductivity of a solution is, as we have seen, dependent upon the number of ions present, their velocity, their mass and volume, and the viscosity of the solution. Since the temperatures at which the dilute solutions freeze are approximately only one-fourth of a degree or less below the freezing point of pure water—the temperature at which the conductivity measurements were made—we must conclude that the number of ions present and their velocities are in the two cases the same. Similarly, the viscosity of the solutions is the same in both measurements and, therefore, the friction between solvent and ion will vary directly as the surface of the latter.

We have shown that most metallic ions in solution have great hydrating power, and that the degree of hydration varies inversely with the atomic volume of the ion. Those ions which have the greatest hydrating power are those which have the smallest atomic volumes, and should, therefore, if there were no hydration, meet with less friction in their movements through the solution. They should have greater migration velocities, while exactly the opposite results are found.

A comparison of the values of α for a dilute solution of the strong acids shows that the dissociation as measured by conductivity is greater in every case than the dissociation measured by the freezing point method. In the more concentrated solutions the observed freezing point lowerings are higher than the molecular lowerings calculated from conductivity. This is due to the fact that the molecules or ions of those acids have considerable hydrating power, and we obtain in concentrated solutions results of the same character as with the salts.

Summary.

1. The freezing point lowerings and the conductivities of solutions of a number of electrolytes, over a wide range of concentration, have been carefully redetermined.

2. We observe that the molecular lowerings of the freezing point of all the electrolytes studied passes through a very pronounced minimum at concentrations ranging from 0.1 to 0.25 normal. The molecular lowerings calculated from the dissociation, as measured by conductivity, decrease regularly from the most dilute to the most concentrated solutions.

3. The magnitude of the molecular lowerings produced by molecular quantities of different salts varies directly as the number of molecules of water with which those salts crystallize from solution. The magnitude of the hydrating power of salts in solution is, in turn, proportional to the amount of water of crystallization.

4. That the ions have very great hydrating power is shown by the values of M and H for the different salts. The total amount of combined water decreases with increase in concentration, passes through a minimum, and then increases regularly with increase in concentration. The amount of water held in combination by one molecule of a salt is very large in the more dilute solutions where the ions predominate. It decreases rapidly with decrease in dissociation, and approaches a constant value at greater concentration.

5. The hydrating power of a salt is, primarily, a function of the cation. The results show that two salts which crystallize with the same amounts of water of crystallization and contain a common cation exhibit hydrating power of the same order of magnitude.

6. It has been found that the hydrating power of a cation is an inverse function of its atomic volume. Those cations which have the smallest atomic volumes have the greatest hydrating power, and *vice versa*. We may state the relations thus: *The hydrating power of the ions is a function of their atomic weights.*

7. Furthermore, we have found that those cations which have the greatest migration velocities exhibit, also, the smallest hydrating power, and *vice versa*. This probably accounts for the apparent anomaly which exists in the relation between the migration velocities of the ions and their atomic weights and atomic volumes. The influence upon the migration

velocity of the hydration of those ions with small atomic volumes is greater than that of the small hydration of those ions which have large atomic volumes.

8. In the case of every salt it has been found that the dissociation in the dilute solutions, as measured by the conductivity method, is *less* than that calculated from the freezing point lowering. Since the freezing point and conductivity measurements of the dilute solutions were made at approximately the same temperature, the number of the ions present, their velocities, and their hydration are practically the same in both cases. The solutions have, likewise, the same viscosity. Therefore, the friction between the solvent and ion will vary directly as the surface of the latter. This being the case, the greater the dilution, the greater will be the complexity of the hydrate, and, consequently, its surface. We should expect to find, therefore, a greater abnormality in the dissociation, as measured by the two methods, the greater the dilution at which the measurements are made. The results show this to be the fact.

It is only in case of those salts which crystallize in the anhydrous condition that we obtain comparable values for the dissociation, as measured by the two methods. These values are found only in those concentrations which lie close to that concentration which gives the minimum molecular lowering.

JOHNS HOPKINS UNIVERSITY,
May, 1907.

NOTE ON THE ARTICLE ENTITLED "STUDIES IN CATALYSIS" BY S. F. ACREE.[1]

BY JULIUS STIEGLITZ.

The substantial similarity in the principal theoretical conclusions reached by me, as set forth in an article[2] to be published in the January number of THIS JOURNAL, and in the paper by S. F. Acree, which has just reached me, compels me to add the following statement of facts in the interest of the question of priority and of historical truth:

[1] THIS JOURNAL, **38**, 253 (1907).

[2] This article was received September 13th, but it has been impossible to arrange for its publication before January. EDITOR.

(1) In my address on "The Relations of Organic Chemistry to other Sciences, a Study in Catalysis," given in September, 1904, before the Congress of Arts and Sciences in St. Louis, and published in the report of the Congress, Vol. IV., pp. 276–284, the leading ideas of the theory of catalysis, as now put forth again by Acree without due acknowledgment, were already presented. In that address, the first vital and decisive step was taken to depart from the old idea that catalytic action can be studied only in reactions which complied with the three fundamental principles so long held regarding catalysis, *viz.*, that the acceleration is proportional to the concentration of the catalytic agent, that, in particular, the catalytic agent must appear to act by its presence simply and not to form a compound in quantity with any of the components, and, finally, that the condition of equilibrium in a reversible reaction must not be measurably changed by the presence of the catalytic agent. I quote the following introductory statement: "These three properties have been assumed to be necessary and typical characteristics of catalytic action. But in this investigation, in order not to overlook, possibly, the real answer to our problem, the vital fact of *acceleration*[1] alone was considered characteristic, and it was left to the rigorous application of fundamental well-known laws of chemistry to develop why, *incidentally*,[1] in this and similar cases the equilibrium is not disturbed sensibly and why the catalyzing acid appears to have no share in the reaction. From this point of view....., the most fundamental fact concerning acids was recalled, the fact that they have the power to form *salts*[1] with bases and oxides, etc." Leaving the old beaten track, then, and taking the question of *acceleration* in a positive or negative sense (p. 279) as the *keynote of all catalytic action*, we studied reactions where, by a combination of a large part of the catalyzer with a reacting component (the imidoesters), we could make "quantitative measurements of all important factors" and could *prove our point* that the acceleration, positive or negative (p. 280), is, *as a matter of experiment, due to salt and ion formation* (p. 279, last lines). Then it was shown (p.

[1] Italics did not appear in the original statement; they were then not necessary.

280), the catalysis of methyl acetate[1] and the esterification of acetic acid[1] being used as illustrations, that the simple application of our common laws of equilibrium to the proved fundamental idea of salt formation led, mathematically and chemically, directly to the three principles mentioned above, *in the case of very weak bases*, like methyl acetate, *when the amount of salt formation lies beyond the scope of our methods of experimental measurement.* For all other cases, the three fundamental principles consequently do not apply and in *no* case do they apply rigorously (p. 282)![2] Having developed and established this theory of catalysis in a fundamental case, we considered all similar actions to be simply matters for experimental verification (p. 284).

This, then, is the theory of catalysis brought out with experimental confirmation by myself, and, stripped of all purely verbal methods of presentation and mathematical and experimental illustrations, *there is not one single new principle presented in Acree's paper.*[3] The mathematical developments, the reactions studied, and the methods used are simply variations and imitations *ad casum* of the fundamental ones given at the Congress. It should be added that Mr. Acree's attention was specifically called to the printed report of this address in December, 1906.

(2) Mr. Acree spent the summer quarter (three months) of 1905 in the chemical laboratory of the University of Chicago, coming—I quote his words— "to get my (Stieglitz's) methods," and discussing freely and with my consent with my collaborators, whose work was already completed, the ideas and investigations carried on in our laboratory. As the St. Louis address had been given the year before and as Mr. Acree is one of our own Doctors of Philosophy, we had no fear of untoward results. With the idea of presenting all the experimental applications, and especially of working out a number of important secondary phases of the question (salt effects,

[1] These were treated as oxonium bases, exactly as Acree has also now done.

[2] *y* is dropped in the formulas.

[3] See his conclusions (p. 355) and the assertions in italics, pp. 259 and 348. Although called the *fourth* paper on catalysis by him, *it is noteworthy that the principles were "discovered" only after he had my paper in printed form before him.* My *first* paper on catalysis (St. Louis address) contained my principles.

etc.) quantitatively and presenting the material complete in all details, the question of the publication of these results was not considered urgent, as we felt we were fully protected in our field by the address—just as we are protected now.

(3) In an address given before the Chemical Club of Johns Hopkins University, April 6, 1907, which Mr. Acree attended, the experimental results obtained in the seven or eight investigations enumerated above[1] were presented, the results confirming my ideas in all respects.

(4) Mr. Acree was kind enough to notify me some weeks ago that he intended publishing a paper on catalysis and to tell me something of the facts he had "re"-discovered. At the time I called his attention to the fact that all those "new principles" modifying our views of catalysis had been discovered and already reported upon in 1904 at the Congress and that I would call attention to this fact if I was not satisfied with his presentation of the case. Since he assured me that he was most anxious to give me full credit for what I had done, I am certain that he will not take this clearer statement of facts in my own words amiss. No doubt he has sought to fulfill his promise, and by this statement I do not wish to reflect in any way unnecessarily on him, but as his paper is a long one, and as, *at the vital points*, he has seen fit to make no mention of my having arrived previously at the same theoretical results and has obscured the issue by giving credit to my paper *for only part of its contents*, I have felt it necessary to call attention to these facts, freed from all obscurities.

CHICAGO, Sept. 10, 1907.

STUDIES IN BROMINATION.

[SIXTH COMMUNICATION ON CATALYSIS.]

BY S. F. ACREE, J. M. JOHNSON, AND SIDNEY NIRDLINGER.

The notice of Cohen and Cross[2] on "The Mechanism of the Bromination of Acylamino Compounds" makes it necessary for us to point out that we have been studying such catalytic reactions in this laboratory during the past two years. In pre-

[1] See the paper to be published in the January number of THIS JOURNAL.

[2] P. Chem. Soc., **23**, 148.

vious articles by Acree and Johnson[1] it was shown quantitatively that these reactions proceed as follows:

$$\left.\begin{array}{l}(1)\ CH_3CONHC_6H_5+Br_2 \\ (2)\ CH_3CONBrC_6H_5+HBr\end{array}\right\} CH_3CONHBr_2C_6H_5 \xrightarrow[A]{} (3)\ CH_3CONHC_6H_4Br+HBr,$$

the reactions being exactly the same as those reported by Jackson and Clarke,[2] and by Fries—[3]

$$(CH_3)_2NC_6H_5+Br_2 \rightleftarrows (CH_3)_2NBr_2C_6H_5 \longrightarrow (CH_3)_2NHBrC_6H_4Br \rightleftarrows (CH_3)_2NC_6H_4Br+HBr.$$

The reaction products of (2) are the chief ones in alkaline solution, while those of (3) are the end products in acid solutions. The velocity of formation of the products of (3) was proved quantitatively to be

$$\frac{dx}{dt}=K_{trans}\times(C_{hal}-x)\times C_H\times C_{Br}=K_{trans}\times(C_{hal}-x)\times C_H^2=K_{trans}\,C_A,$$

in which C_{hal} is the initial concentration of the acylhalogenaminobenzene, and the other terms have the usual significance. The intermediate product, A, and such products as *enzyme-ester*,[4] $CH_3COOR.\overset{+}{H}$, $(CH_3)_2=\overset{+}{N}HOH$, $(C_6H_{11}O_5)_2\overset{+}{O}H$, $CH_3C(\bar{O})(OH)(NH_2)$, etc., are the *active* forms mentioned by Arrhenius[5] and others in many catalytic reactions.

The success of Cohen and Cross in isolating the compound $CH_3CONHBr_2C_6H_4CH_3$ is an interesting confirmation of our views. Mr. Nirdlinger has been able to obtain from the compound $CH_3CON(CH_3)C_6H_5$ and bromine the addition product $CH_3CONBr_2(CH_3)C_6H_5$ in not quite pure state. The substance liberates iodine from iodides, oxidizes alcohol to acetaldehyde, and behaves as is to be expected of such products. The investigation is being extended to the reactions involved in the formation and rearrangement of such compounds as phenyl-

[1] THIS JOURNAL, **37**, 410; **38**, 265.
[2] *Ibid.*, **34**, 261; **36**, 409.
[3] Ann. Chem. (Liebig), **346**, 128.
[4] Acree and Hinkins: THIS JOURNAL, **38**, 372.
[5] Z. physik. Chem., **4**, 233.

hydroxylamine, phenylnitramine, phenylsulphaminic acid, and other analogous cases.

JOHNS HOPKINS UNIVERSITY,
October 20, 1907.

REVIEWS.

INTRODUCTION TO METALLURGICAL CHEMISTRY FOR TECHNICAL STUDENTS. By J. H. STANSBIE, B.Sc. (Lond.), F.I.C., Associate of Mason University College and Lecturer in the Birmingham Municipal High School. Second edition. New York: Longmans, Green & Co. pp. 252. Price, $1.25 net.

A very simple, clear, little manual compiled for the use of students of metallurgy in technical evening schools. E. R.

JAHRBUCH DER CHEMIE. Bericht über die wichtigsten Fortschritte der reinen und angewandten Chemie. Unter Mitwirkung von H. BECKURTS, Braunschweig; C. A. BISCHOFF, Riga; M. DELBRÜCK, Berlin; J. M. EDER, Wien; TH. FISCHER, Berlin; P. FRIEDLÄNDER, Wien; C. HAEUSSERMANN, Ludwigsburg; A. HERZFELD, Berlin; K. A. HOFMANN, München; J. LEWKOWITSCH, London; A. MORGEN, Hohenheim; M. NIERENSTEIN, Liverpool; F. QUINCKE, Leverkusen; O. SACKUR, Breslau; K. SPIRO, Strassburg i. E.; herausgegeben von RICHARD MEYER, Braunschweig. XVI. Jahrgang, 1906. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. 1907. pp. 638. Unbound 16 M.; bound 17 M.

The Jahrbuch is always welcome and always profitable to the reader. It is a book that a chemist can sit down and read and be interested in. If he is specially informed in the field of physical chemistry, he will, of course, learn more from those chapters that deal with other branches of chemistry. If he is an "organic chemist" he will do well to read the chapters on physical chemistry and inorganic chemistry. He is sure to find much that in his daily reading he has missed. So, too, the chemist who is not engaged in technical work will do well to read the chapters that deal with technical matters.

The writer of this notice has examined this volume of the Jahrbuch with some care and especially those parts of it which treat of matters more or less familiar, and is glad to be able to say that those who have prepared the reports appear to have used good judgment in the selection of material. I. R.

STUDIES IN PLANT AND ORGANIC CHEMISTRY AND LITERARY PAPERS. By HELEN ABBOTT MICHAEL (HELEN C. De S. ABBOTT) with Biographical Sketch. Cambridge, Mass.: Riverside Press. 1907. pp. 423. Price, $2.50.

The scientific "gifted amateur," though little known in this country, and practically not at all on the continent of Europe, has always flourished in England, as the names of Darwin, Romanes, De la Rue, Lord Rayleigh, and many

others testify. These investigators have set standards for the professional worker, but they were "amateurs" because their scientific activities were in no way connected with their means of livelihood. Mrs. Michael was an amateur in the same sense of the word, and, so far as the writer is aware, she shared with Madame Curie the distinction of being the only woman devoted to chemistry for its own sake. Since M. Curie's death, Madame Curie, having accepted an official appointment, has become a " professional."

The book under review contains a biographical sketch of Mrs. Michael by Nathan Haskell Dole, her collected chemical publications, dealing, as is well-known, chiefly with plant constituents, and certain papers relating to literature and art, subjects to which she chiefly devoted her attention during the later years of her life.

The news of Mrs. Michael's untimely death was received by chemists generally, including those to whom, like the reviewer, she was personally unknown, with feelings of sincere regret and respectful sympathy for her husband and relations. The issue of this volume, which forms an admirable memorial of her work, will serve to revive and renew these sentiments.

J. B. T.

RADIOAKTIVE UMWANDLUNGEN. Von E. RUTHERFORD, Professor der Physik an der McGill Universität in Montreal. Übersetzt von M. LEVIN. Mit 53 eingedruckten Abbildungen. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. 1907. pp. 285.

This is the translation into German of Rutherford's well-known Yale lectures. The author states that "in arranging the chapters of the present volume, the order in which the subject was dealt with in the lectures has been closely followed, but as our knowledge of the subject is increasing so rapidly, I have thought it desirable to incorporate the results of the many important investigations which have been made since the lectures were delivered. This is especially the case in the chapter dealing with the α-rays, to which much attention has been devoted in the past year on account of the important part they play in radioactive transformations. * * * * As some months have elapsed since the appearance of the English edition, it has been thought desirable to make a brief reference in the form of footnotes to the more important advances made in the interval."

The above quotation from the preface will serve to show that the work has been brought up to date. The fact that it is written by Rutherford guarantees it as a standard in the field of radioactivity. As the work has already been reviewed

in THIS JOURNAL,[1] it is only necessary, in the present connection, to call attention to the appearance of the up-to-date German edition. H. C. J.

SOLUBILITIES OF INORGANIC AND ORGANIC SUBSTANCES. A HANDBOOK OF THE MOST RELIABLE QUANTITATIVE SOLUBILITY DETERMINATIONS. Recalculated and compiled by ATHERTON SEIDELL, Ph.D. (J. H. U.), Chemist, Division of Pharmacology, Hygienic Laboratory of the U. S. Public Health and Marine Hospital Service, Washington, D. C. Formerly assistant chemist, Bureau of Chemistry, U. S. Department of Agriculture. New York: D. Van Nostrand Company, 23 Murray and 27 Warren Sts. 1907. pp. 367.

The author states that "The following features have been considered of chief importance in preparing the present compilation: Completeness of the data, reliability of the determinations, uniformity in expression of results, convenience of arrangement of material, and the indexing of the cross references to tables. The material has been collected almost entirely from the original sources, and not from text-books or works of reference. The plan followed has been to search diligently the tables of contents or indices of twenty-five of the principal chemical journals issued since 1875, and to consult all articles in these as well as in other journals to which references could be obtained."

The above program outlines the general plan of the work. A glance at the contents indicates that the plan has been followed conscientiously. More careful attention, however, to linguistic matters would have improved the book. Whatever else may be said of such a work, it is clear that an enormous amount of drudgery is involved in its preparation. To have such data as are contained in this volume in a compact form is of value to investigators and also to technical chemists.

H. C. J.

[1] **37**, 661 (1907).